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# ***Catenated Organic Compounds of Silicon, Germanium, Tin, and Lead***

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## **I**

### **INTRODUCTION**

Chemists have only relatively recently been made aware of the extent to which catenation may be observed throughout the entire periodic table.

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Far from being limited to carbon or other nonmetallic elements, catenation is now taken as a matter of course in many compounds of the transition metals.

The term, catenation, is a rather imprecise one, referring to a whole collection of properties which are observed when an element forms stable bonds to itself. One commonly encounters the statement that the tendency toward catenation falls off sharply among the Group IVB elements from carbon to lead. The statement is reasonably correct, but conveys little about the actual nature of the differences which do exist in the chemical characteristics of the catenated compounds. The present survey hopes to afford a clearer view of the properties of organic derivatives of catenated Group IVB elements. Each element from silicon to lead will be considered in a separate section, followed by a section bringing together the comparisons that can be made among the elements. It is expected that the last section will have the most interest for a wider audience, hence the separate treatment.

The authors have attempted to make the coverage complete until approximately the middle of 1965. The tables for the sections on germanium, tin, and lead contain all derivatives known to the authors which have been reasonably well characterized. The tabulation of silicon compounds is much more limited due to the fact that the number of known derivatives is unwieldy, and many of the compounds have been tabulated in other review articles. A further statement concerning the coverage is contained in the silicon section. Strictly inorganic derivatives have been excluded from the tables, but may be mentioned in the text when they exemplify a significant fundamental property of the catenated types. Mixed types, i.e., those containing Si—Ge, Ge—Sn, etc., bonds with or without attached organic groups, have been treated in the same manner as the inorganic derivatives.

It is a pleasure to acknowledge a number of review articles and bibliographies (1-16) which have been of considerable aid during the course of this writing. Hopefully, the present treatment and those that have gone before will be able to stimulate the undertaking of original investigations in an area which the authors have found to be fruitful and intensely rewarding.

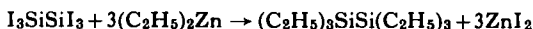
## II

### SILICON

#### A. Historical

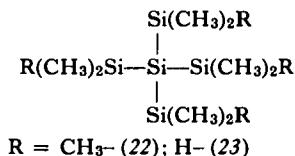
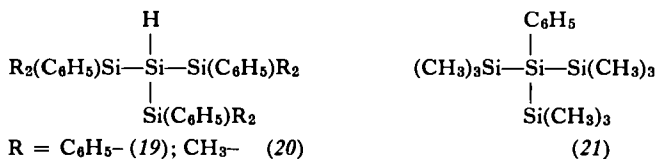
Six years after the preparation of the first organosilicon compound (tetraethylsilane), Friedel and Ladenburg reported (17) the synthesis of the

first catenated derivative of this class of compound, namely, hexaethyl-disilane. Their procedure involved the reaction of hexaiododisilane with diethylzinc.



Since this original synthesis the preparation and properties of a vast number of disilanes have been investigated (2). Although several organopolysilanes containing more than two contiguous silicon atoms were first prepared by Kipping (14) more than 40 years ago, the study of these compounds was for a number of years largely confined to the disilane derivatives.

In recent years, considerable attention has been directed toward a study of the more highly catenated linear and cyclic polysilanes (1, 2, 14, 18). An interesting facet of this recent work involves the preparation of branched polysilanes such as those illustrated below.



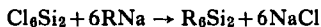
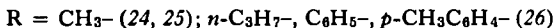
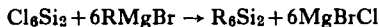
From the rapidly growing population of the area of organopolysilanes, it would seem that neither the chain length nor the degree of branching is a limiting factor in the stability of these compounds. Thus, it would appear that the formation of a homologous series of organopolysilanes, somewhat analogous to those of saturated hydrocarbons, will be limited mainly by the interest of the investigators, the synthetic methods available, and the lack of exploitation of new preparative methods.

## B. Preparation

Since the polysilanes are synthesized by essentially the same methods used for the lowest member of the class, i.e., the disilanes, this section will describe the various methods used for the synthesis of disilanes followed by the applicability of each method to the synthesis of higher polysilanes.

### 1. From Hexahalodisilanes and Organometallic Reagents

The first method employed for the synthesis of an organodisilane utilized the reaction between hexaiododisilane and diethylzinc (17). Later investigations employed other organometallic reagents and demonstrated the versatility of this method.

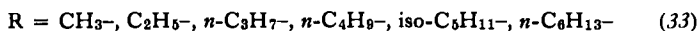
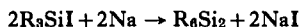


Steric factors can become important in these reactions since disilanes can be obtained from *m*- and *p*-tolylmagnesium bromide and  $\text{Cl}_6\text{Si}_2$  but not from *o*-tolylmagnesium bromide (26). Also, disilanes cannot be prepared under Wurtz-type coupling conditions by treatment of alkyl or aryl halides with sodium in the presence of hexachlorodisilane (29). Such reactions give only the tetrasubstituted monosilane.

The reactions of halo polysilanes with organometallic reagents usually proceed with some Si—Si bond cleavage (17, 26, 29, 30, 31), and these reactions have little synthetic value for the preparation of higher polysilanes. Thus, from the reaction between  $\text{Cl}_8\text{Si}_3$  and phenylmagnesium bromide no trisilane product was obtained, and only tetraphenylsilane and hexaphenyl-disilane were isolated (26). On the basis of reactions of this type, it was postulated (26) that the reactivity of the Si—Si bond in halogenated polysilanes increases as the number of silicon atoms increases.

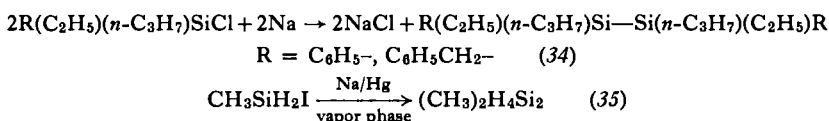
### 2. From Organohalosilanes and Metals

The most straightforward route to organodisilanes involves the coupling of a triorganosilyl halide by treatment with sodium (2, 32). This method was first employed by Schlenk (32) while attempting to prepare the free triphenylsilyl radical and later by Kipping (32). This procedure is equally applicable to the preparation of mixed disilanes, and variations of the reaction conditions have been reported. In particular, the formation of



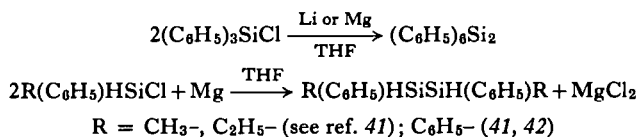
hexamethyldisilane has been accomplished by using numerous modifications. Recent workers have reported the coupling of chlorotrimethylsilane

using sodium-potassium alloy (36, 37, 38), potassium metal (36, 38), and a sodium- $\text{AlCl}_3$  system (36). In addition to variations of the metal component,



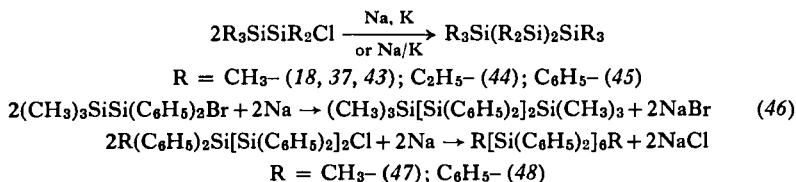
the elimination of solvent (38), the use of an ethyl acetate catalyst (18), and the use of rapid stirring (36, 39), ultrasonics (39), and autoclaves (18) are methods which have been utilized in the synthesis of hexamethyldisilane.

Recently, the coupling of halosilanes with lithium (40) or magnesium (41, 42) in tetrahydrofuran (THF) has been carried out. While the magnesium coupling reaction is useful for the production of functional

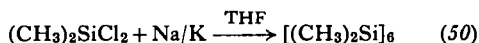


disilanes, it is limited to the preparation of phenyl-containing compounds.

Practically all of the above reactions have, with some variation in the halosilane, been applied to the synthesis of higher polysilanes. Reactions which are strictly analogous to those described above have been employed in the synthesis of tetra- and hexasilanes.



Reaction of the appropriate diorganodihalosilane with metals gives cyclosilane derivatives such as octaphenylcyclotetrasilane (14), decaphenylcyclopentasilane (14), dodecaphenylcyclohexasilane (14), and dodecamethylcyclohexasilane (14, 49, 50). The above reactions, as well as the

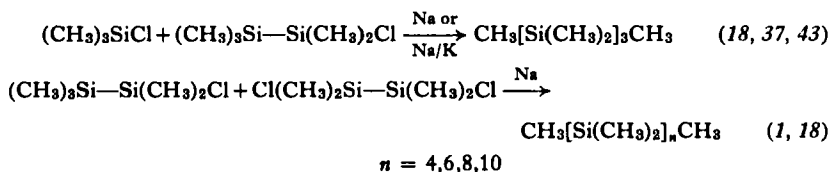


formation of cyclosilanes by the cyclization of  $\alpha, \omega$ -dihalopolysilanes with metals, have been recently reviewed (14).

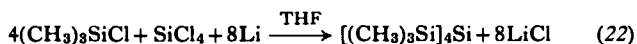
The usefulness of the metal coupling reaction has been increased by employing a mixture of halosilanes and/or  $\alpha, \omega$ -dihalopolysilanes. Thus, the



synthesis of a homologous series of methylated polysilanes of the type  $\text{CH}_3[\text{Si}(\text{CH}_3)_2]_n\text{CH}_3$  ( $n = 2, 3, 4, 5, 6, 8, 10$ ) has been reported (18) using reactions of the following type:



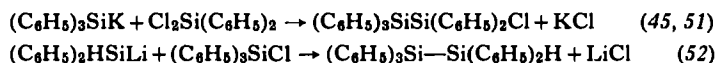
A mixture of chlorotrimethylsilane and silicon tetrachloride was used in the recent synthesis of tetrakis(trimethylsilyl)silane, the first known organopolysilane containing a tetrasilyl-substituted silicon atom. A similar



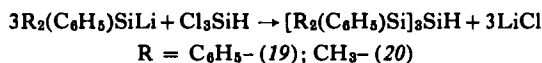
reaction with chlorodimethylsilane gave another member of this new class of compounds, tetrakis(dimethylsilyl)silane (23).

### 3. From Silylmetallic Reagents

The synthesis of disilanes *via* silylmetallic reagents has been the subject of several recent reviews (4, 5, 14). Since the silylmetallic reagents are prepared by the reaction of metals with triorganohalosilanes ("direct" preparation) or hexaorganodisilanes, the reagents are chiefly used for the synthesis of unsymmetrical rather than symmetrical disilanes.

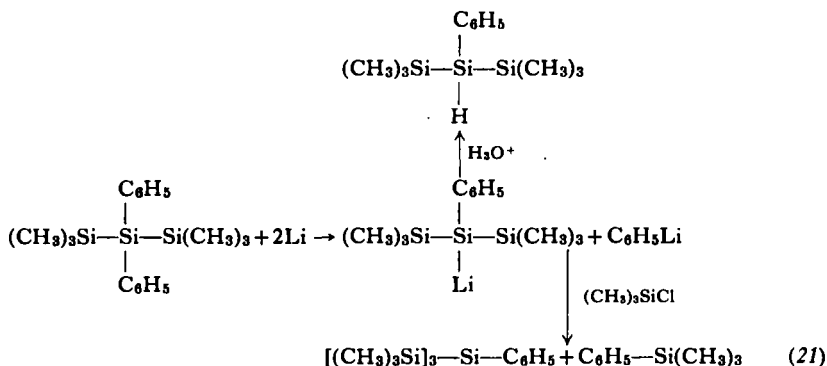


The preparation of a variety of higher polysilanes using silylmetallic reagents has been described (4, 5, 14). More recently, silylmetallics have been successfully employed in the synthesis of branched polysilanes. Treatment of silicochloroform with either triphenyl- or dimethylphenylsilyllithium gives the corresponding tris derivatives.

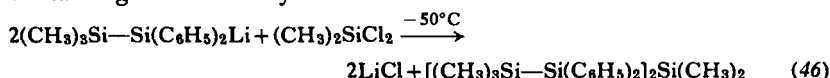


Likewise, reaction of chlorotrimethylsilane with the silyllithium reagent resulting from cleavage of a silicon-phenyl group of bis(trimethylsilyl)-

diphenylsilane gives tris(trimethylsilyl)phenylsilane, whereas acid hydrolysis of this reagent gives bis(trimethylsilyl)phenylsilane.

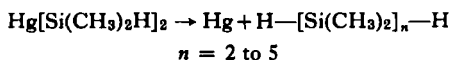


Decaphenyltetrasilane and 1*H*-heptaphenyltrisilane were obtained from triphenylsilyllithium and 1,2-dichlorotetraphenyldisilane after treatment of the reaction mixture with lithium aluminum hydride (53). The usefulness of these reagents is illustrated further by the synthesis of polysilanes containing "mixed" silylene units.



The preparation of polysilanes by the reaction of intermediately formed silylmetallics, derived from cyclosilanes, will be discussed in the next section.

Polysilanes have been prepared by the pyrolysis of a variety of silylmetallic compounds (54).

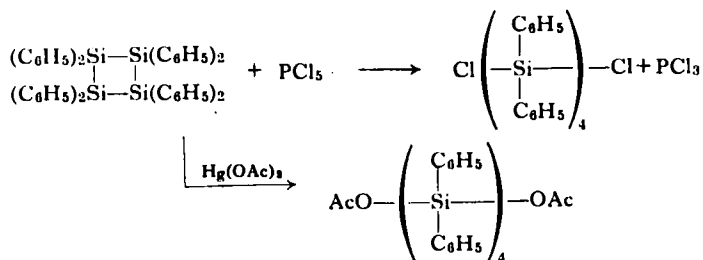


While experimental details are lacking, these reactions appear promising for the synthesis of higher polysilanes.

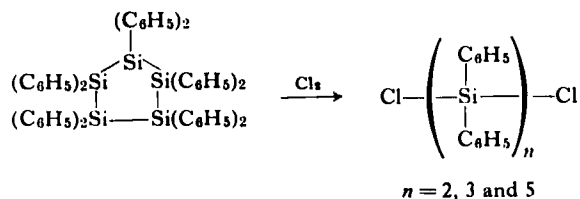
#### 4. From Cyclosilanes

One of the most useful methods for the synthesis of polysilanes involves the cleavage of cyclosilanes with a variety of reagents. Thus, octaphenylcyclotetrasilane has been found to react with halogens, hydrogen halides, inorganic halides, and a wide array of halogenated hydrocarbons to give halogenated tetrasilane (and in some instances disilane) derivatives (14). Reaction of octaphenylcyclotetrasilane with mercuric acetate gives the

corresponding 1,4-diacetoxy derivative (55). This latter reaction suggests that other inorganic salts may provide access to additional silicon-functional polysilanes.

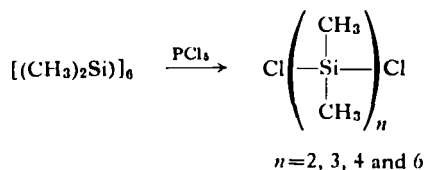


Although decaphenylcyclopentasilane is more stable to halogenated hydrocarbons and inorganic salts, it is cleaved by chlorine, bromine, and phosphorus pentachloride to give  $\alpha,\omega$ -dihalopolysilanes (14).

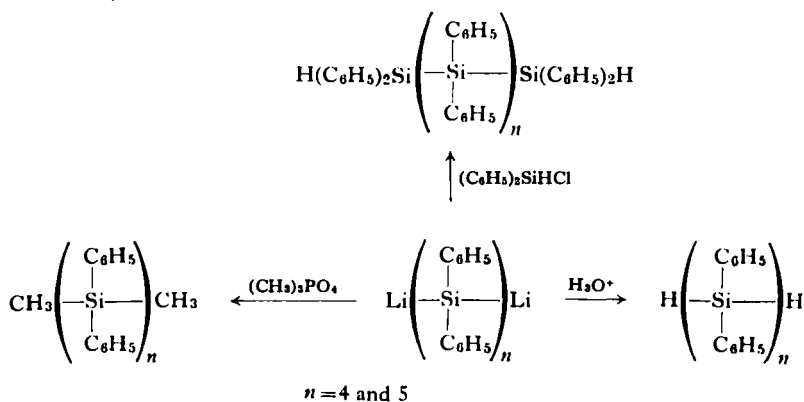


Recent work on the ring cleavage of dodecamethylcyclohexasilane (14) with halogens and halogenating agents indicates the utility of this cyclosilane for the preparation of silicon-functional polysilanes. Reaction of dodecamethylcyclohexasilane with iodine (50) has been reported to give 1,6-diiodododecamethylhexasilane as the major product; however, no experimental details were given. Chlorine (20) has also been employed; however, in this case rapid degradation of the initially formed  $\alpha,\omega$ -dichloro compound occurs. Suitable control of the experimental conditions allows one to obtain good yields of 1,2-dichlorotetramethyldisilane (20). A useful approach to the preparation of  $\alpha,\omega$ -dichloropermethyated polysilanes involves the reaction of dodecamethylcyclohexasilane with phosphorus pentachloride in carbon tetrachloride or *sym*-tetrachloroethane solvent (14, 23, 56). The use of phosphorus pentachloride and a petroleum ether (b.p. 60°–70° C) solvent has been even more successful for the preparation of these  $\alpha,\omega$ -dichloro derivatives (57). Halogenation of dodecamethylcyclohexasilane is also effected with refluxing *sym*-tetrachloroethane (14, 56).

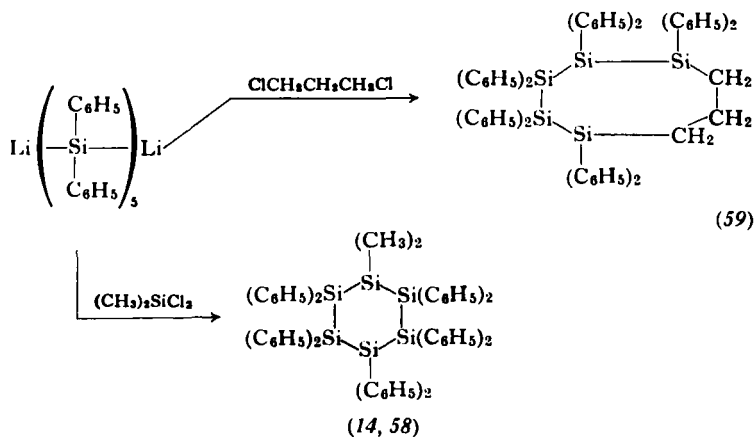
The reaction of octaphenylcyclotetrasilane (14, 47) and decaphenylcyclopentasilane (14, 58) with lithium gives the corresponding  $\alpha,\omega$ -dilithio



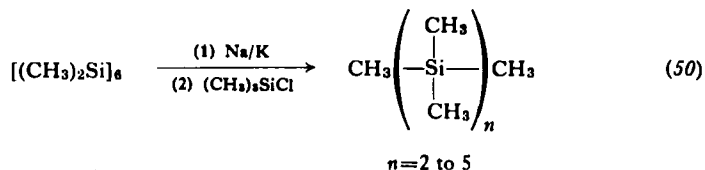
compounds. These latter reagents can be utilized under a variety of reaction conditions (14, 47).



The usefulness of these dilithio reagents is illustrated further by the preparation of other cyclic organosilicon and cyclosilane derivatives (see also Section VI on General Trends).

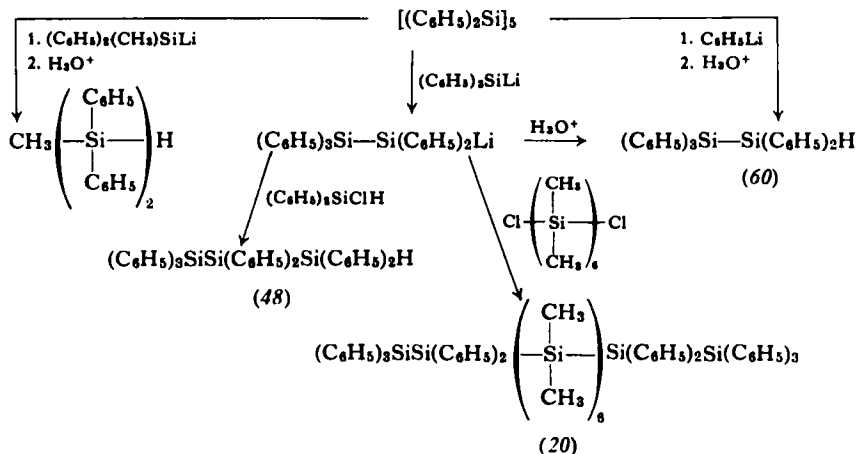


Likewise, cleavage of dodecamethylcyclotetrasilane with sodium-potassium alloy followed by derivatization with chlorotrimethylsilane gives a mixture of linear permethylated polysilanes. Presently, the investigations concerning the synthetic utility of this cyclosilane are in a preliminary stage, and



reactions as obvious as the derivatization of the above silylmetallic mixture with  $\text{R}_2\text{SiCl}_2$  compounds (an approach to other permethylated cyclosilanes) have not been reported.

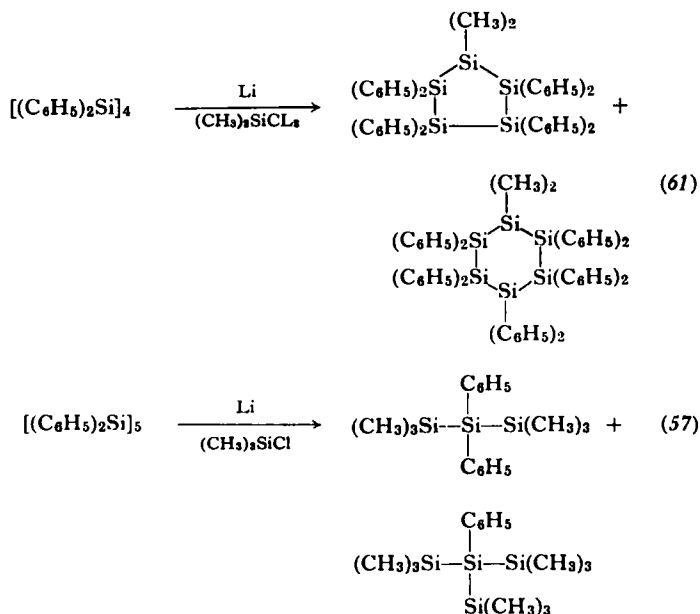
The reaction of cyclosilanes with organometallic and organosilylmetallic reagents gives synthetically useful polysilylmetallic derivatives (see also Section VI on General Trends).



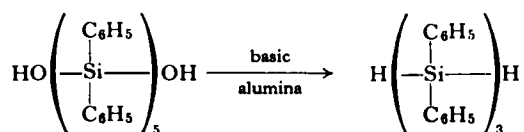
In addition, the cleavage of octaphenylcyclotetrasilane and decaphenylcyclopentasilane with lithium in the presence of chlorosilanes has provided access to a variety of polysilane derivatives. Other reactions describing the use of cyclosilanes for the preparation of polysilanes have been thoroughly reviewed (14).

The conversion of silicon-functional polysilanes (obtained from cyclosilanes) to other polysilane derivatives is also possible. Thus, reaction of

decaphenylpentasilane-1,5-diol with basic alumina provides the most direct route to 1*H*,3*H*-hexaphenyltrisilane (14, 58, 61*a*). The majority of



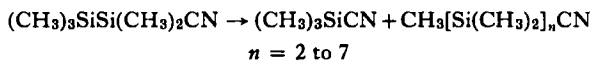
these conversions involve standard reactions of the functional group and will be discussed more fully in the section on Chemical Properties.



### 5. Miscellaneous

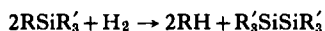
The higher boiling residues obtained in the "Direct Synthesis" of methylchlorosilanes (from elementary silicon and methyl chloride) include a variety of compounds which contain silicon-silicon bonds. A particularly useful fraction (b.p. 150°-160° C) contains methylchlorodisilanes of the type,  $(\text{CH}_3)_n\text{Cl}_{6-n}\text{Si}_2$ . The use of this fraction for the preparation of disilanes has been described (2, 62-65); however, few applications leading to the formation of higher polysilanes have been reported.

Recently, the condensation-polymerization reaction of a mixture of methylchlorodisilanes has been reported (66). This reaction is catalyzed by silver cyanide, and treatment of the reaction mixtures with methylmagnesium bromide gave hexamethyldisilane, octamethyltrisilane, decamethyltetrasilane, and dodecamethylpentasilane. The condensation-polymerization of pentamethyldisilanyl cyanide and heptamethyltrisilanyl cyanide has also been reported (66). The products of these latter reactions are trimethylsilyl cyanide and higher methylcyanopolysilanes. This scheme allows the preparation of polysilanes in the absence of metals and promises to be an extremely useful synthetic method.



The preparation of disilanes and higher polysilanes from divalent silicon species has been reported recently. Reaction of dimethylsilylene  $[(\text{CH}_3)_2\text{Si}]$  with trimethylsilane gave pentamethyldisilane (67), while with isobutylene, 1,1,2,2,3,3,4,4,5,5-decamethyl-1,2,3,4-tetrasilacyclohexane was isolated (68).

Hexaalkyldisilanes have been obtained from the hydrogenolysis of tetraorganosilanes at high pressures and temperatures (2).



Hydrogenolysis of octaphenylcyclotetrasilane in the presence of chromium-containing catalysts gave a low yield of 1*H*,4*H*-octaphenyltetrasilane (14). In their present state, these hydrogenolysis reactions appear to be of little use for the synthesis of higher polysilanes.

Heating tris(trimethylsilyl)phosphine (69) or oxidation of *sym*-bis(trimethylsilyl)hydrazine (70) results in the formation of hexamethyldisilane. Again no similar reactions have been reported with higher polysilanes.

Recently, polysilanes have been prepared by the photolysis of SiH compounds (70*a*).

In view of the vast number of disilane derivatives which have been prepared, a comprehensive tabulation of these compounds in this work was considered impractical. We have, however, attempted to include in Table I (71-100, etc.) all disilanes prepared since 1958 together with numerous historically or synthetically significant derivatives prepared prior to this date. This table together with that previously reported (14) should, however, provide a comprehensive survey of the known higher polysilanes.

TABLE I  
ORGANOPOLYSILANES

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Disilanes</i>			
C <sub>2</sub> H <sub>10</sub> Si <sub>2</sub>	1,2-Dimethyldisilane	(49°)	35, 80a
C <sub>3</sub> H <sub>9</sub> Cl <sub>3</sub> Si <sub>2</sub>	1,1,1-Trichlorotrimethyldisilane	(146°–152°)	65
C <sub>4</sub> H <sub>12</sub> Br <sub>2</sub> Si <sub>2</sub>	1,2-Dibromotetramethyldisilane	ca. 40° (79°–82°/30 mm)	1, 54
C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> Si <sub>2</sub>	1,2-Dichlorotetramethyldisilane	(146°–148°) $n_D^{20}$ 1.4545	20, 56, 71, 72
C <sub>4</sub> H <sub>12</sub> ClFSi <sub>2</sub>	1-Chloro-2-fluorotetramethyldisilane	—	73
C <sub>4</sub> H <sub>12</sub> F <sub>2</sub> Si <sub>2</sub>	1,2-Difluorotetramethyldisilane	(92°–93°) $n_D^{20}$ 1.3837	71, 73
C <sub>4</sub> H <sub>14</sub> Si <sub>2</sub>	1 <i>H</i> ,2 <i>H</i> -Tetramethyldisilane	–92° (88°)	54, 69a, 80a
C <sub>5</sub> H <sub>14</sub> Cl <sub>2</sub> Si <sub>2</sub>	1-Chloro-2-(chloromethyl)tetramethyldisilane	9° (79.5°/17 mm) $n_D^{20}$ 1.4735	1, 64, 74
C <sub>5</sub> H <sub>14</sub> ClFSi <sub>2</sub>	1-(Chloromethyl)-2-fluorotetramethyldisilane	(155°–160°)	74
C <sub>5</sub> H <sub>15</sub> ClSi <sub>2</sub>	Chloropentamethyldisilane	(134°–135.6°) $n_D^{20}$ 1.4430	37, 62, 71
C <sub>5</sub> H <sub>15</sub> FSi <sub>2</sub>	Fluoropentamethyldisilane	(98°–103°) $n_D^{20}$ 1.4031	71, 73, 75
C <sub>5</sub> H <sub>16</sub> Si <sub>2</sub>	1 <i>H</i> -Pentamethyldisilane	(97.5°/715 mm)	67, 69a, 76, 80a
C <sub>6</sub> H <sub>15</sub> NSi <sub>2</sub>	Pentamethyldisilanyl cyanide	(176.4°) $n_D^{30}$ 1.43735	62
C <sub>6</sub> H <sub>15</sub> NOSi <sub>2</sub>	Pentamethyldisilanyl isocyanate	(159.4°–160°) $n_D^{30}$ 1.4337	75
C <sub>6</sub> H <sub>16</sub> Cl <sub>2</sub> Si <sub>2</sub>	(Dichloromethyl)pentamethyldisilane	(73°/10 mm) $n_D^{20}$ 1.4755	77



TABLE I—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Disilanes (continued)</i>			
C <sub>6</sub> H <sub>16</sub> Cl <sub>2</sub> Si <sub>2</sub>	1,2-Bis(chloromethyl)tetramethyldisilane	34° (85°/9 mm)	78
C <sub>6</sub> H <sub>16</sub> I <sub>2</sub> Si <sub>2</sub>	1,2-Bis(iodomethyl)tetramethyldisilane	(104°–105°/3 mm)	78
		$n_D^{20}$ 1.5840	
C <sub>6</sub> H <sub>17</sub> ClSi <sub>2</sub>	(Chloromethyl)pentamethyldisilane	6°–7° (87°–87.5°/58 mm)	64, 77
		$n_D^{20}$ 1.4576	
C <sub>6</sub> H <sub>17</sub> ClHgSi <sub>2</sub>	Pentamethyldisilanylmethylmercuric chloride	69°–70°	18
C <sub>6</sub> H <sub>17</sub> ISi <sub>2</sub>	(Iodomethyl)pentamethyldisilane	(96°–97°/23 mm)	78
		$n_D^{20}$ 1.5110	
C <sub>6</sub> H <sub>18</sub> Si <sub>2</sub>	Hexamethyldisilane	14.2°–14.4° (112.8°–113°)	18, 24, 25, 33,
		$n_D^{20}$ 1.4229	36, 37, 38, 79,
			80
C <sub>6</sub> H <sub>18</sub> O <sub>4</sub> Si <sub>2</sub>	<i>sym</i> -Dimethyltetramethoxydisilane	(86°–87°/30 mm)	69b
		$n_D^{25}$ 1.4166	
C <sub>7</sub> H <sub>18</sub> Si <sub>2</sub>	Vinylpentamethyldisilane	(120°–121°)	81
		$n_D^{20}$ 1.4441	
C <sub>7</sub> H <sub>18</sub> O <sub>2</sub> Si <sub>2</sub>	(Pentamethyldisilanyl)acetic acid	57°	81
C <sub>7</sub> H <sub>19</sub> ClSi <sub>2</sub>	1-(Chloromethyl)-2-ethyltetramethyldisilane	(79°/26 mm)	64
		$n_D^{20}$ 1.4662	
C <sub>7</sub> H <sub>20</sub> OSi <sub>2</sub>	Ethoxypentamethyldisilane	(143.5°–144.5°)	78
		$n_D^{20}$ 1.4229	
C <sub>8</sub> H <sub>18</sub> Si <sub>2</sub>	1,2-Divinyltetramethyldisilane	(69.5°/24 mm)	57
		$n_D^{20}$ 1.4626	
C <sub>8</sub> H <sub>20</sub> Si <sub>2</sub>	Isopropenylpentamethyldisilane	(152°)	82
		$n_D^{20}$ 1.4517	
C <sub>8</sub> H <sub>20</sub> Si <sub>2</sub>	Allylpentamethyldisilane	(155°)	81
		$n_D^{20}$ 1.4505	

$C_8H_{22}Si_2$	1,2-Diethyltetramethyldisilane	(168°–171°) $n_D^{20}$ 1.4440	63
$C_8H_{22}O_2Si_2$	1,2-Diethoxytetramethyldisilane	(169°–170°) $n_D^{20}$ 1.4240	78
$C_8H_{24}N_2Si_3$	Octamethyl-1,3-diaza-2,4,5-trisilacyclopentane	– 18° (70°/13 mm)	83
$C_8H_{24}O_2Si_4$	Octamethyl-1,4-dioxa-2,3,5,6-tetrasilacyclohexane	45°	1
$C_8H_{24}S_2Si_4$	Octamethyl-1,4-dithia-2,3,5,6-tetrasilacyclohexane	111°–112° (sublimes)	83a
$C_8H_{32}Si_2$	1,1,2,2-Tetramethyl-1,2-disilacyclohexane	(175°) $n_D^{20}$ 1.4651	1
$C_9H_{22}Si_2$	But-3-en-1-ylpentamethyldisilane	(171°) $n_D^{20}$ 1.4517	81
$C_9H_{24}Si_2$	1,1,2-Triethyltrimethyldisilane	(192°–194°) $n_D^{20}$ 1.4540	63
$C_9H_{24}O_3Si_2$	1,1,2-Triethoxytrimethyldisilane	(72°–73°/13 mm) $n_D^{20}$ 1.4220	1
$C_{10}H_{18}Si_2$	1 <i>H</i> -2-Phenyltetramethyldisilane	(111.5°–112°/27 mm) $n_D^{20}$ 1.5150	57
$C_{10}H_{20}Si_2$	(Cyclopentadienyl)pentamethyldisilane	(86°/22 mm) $n_D^{20}$ 1.4913	80b
$C_{10}H_{22}Si_2$	1,2-Diisopropenyltetramethyldisilane	(97°–98°/32 mm) $n_D^{20}$ 1.4750	82
$C_{10}H_{22}Si_2$	1,1-Dimethyl-1,1-disiladicyclopentyl	(98°/10 mm) $n_D^{20}$ 1.5049	1
$C_{10}H_{25}BrSi_2$	Bromopentaethyldisilane	(88°/2 mm)	44
$C_{10}H_{26}Si_2$	Tetraethyl-1,2-dimethyldisilane	(207°–212°) $n_D^{20}$ 1.4603	63
$C_{10}H_{26}Si_2$	1 <i>H</i> -Pentaethyldisilane	(78°–83°/1.5 mm) $n_D^{20}$ 1.4608	83b
$C_{10}H_{26}O_4Si_2$	Tetraethoxy-1,2-dimethyldisilane	(101.5°–102°/22 mm) $n_D^{20}$ 1.4200	1
$C_{10}H_{30}OSi_4$	Bis(pentamethyldisilanyl) ether	(214.4°) $n_D^{20}$ 1.4334	62

TABLE I—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (°C)	Reference
<i>Disilanes (continued)</i>			
C <sub>10</sub> H <sub>31</sub> NSi <sub>4</sub>	Bis(pentamethyldisilanyl)amine	(132.5°–134°/40.5 mm) $n_D^{30}$ 1.4556	75
C <sub>11</sub> H <sub>19</sub> BrSi <sub>2</sub>	( <i>p</i> -Bromophenyl)pentamethyldisilane	(131°–133°/9 mm) $n_D^{20}$ 1.5345	81
C <sub>11</sub> H <sub>19</sub> ClSi <sub>2</sub>	( <i>p</i> -Chlorophenyl)pentamethyldisilane	(108°–110°/6 mm) $n_D^{20}$ 1.5223	81
C <sub>11</sub> H <sub>20</sub> Si <sub>2</sub>	Pentamethylphenyldisilane	(95°–95.5°/11 mm) $n_D^{20}$ 1.5084	57, 81, 84
C <sub>12</sub> H <sub>20</sub> O <sub>2</sub> Si <sub>2</sub>	( <i>p</i> -Carboxyphenyl)pentamethyldisilane	148°	81
C <sub>12</sub> H <sub>22</sub> Si <sub>2</sub>	Benzylpentamethyldisilane	(105°–106°/11 mm) $n_D^{20}$ 1.5092	81
C <sub>12</sub> H <sub>30</sub> Si <sub>2</sub>	(1-Methylcyclohexyl)pentamethyldisilane	(83°–84°/0.5 mm) $n_D^{20}$ 1.4812	69a
C <sub>12</sub> H <sub>30</sub> Si <sub>2</sub>	Tetramethyl-2- <i>n</i> -octyldisilane	(80.5°–81.5°/3.5 mm) $n_D^{20}$ 1.4505	69a
C <sub>12</sub> H <sub>30</sub> HgSi <sub>2</sub>	Ethyl(pentaethyldisilanyl)mercury	(100°–104°/0.1 mm). $n_D^{25}$ 1.5353	83b
C <sub>13</sub> H <sub>25</sub> NSi <sub>2</sub>	( <i>p</i> -Dimethylaminophenyl)pentamethyldisilane	44°–46° (137°–138°/5 mm)	81
C <sub>13</sub> H <sub>32</sub> Si <sub>2</sub>	<i>n</i> -Octylpentamethyldisilane	(93.5°–94°/5 mm) $n_D^{25}$ 1.4486	69a
C <sub>14</sub> H <sub>18</sub> Si <sub>2</sub>	1 <i>H</i> ,2 <i>H</i> -1,2-Dimethyldiphenyldisilane	(81°–83°/0.003 mm) $n_D^{20}$ 1.5769	41
C <sub>14</sub> H <sub>42</sub> O <sub>2</sub> Si <sub>6</sub>	Tetramethyl-1,2-bis(pentamethyldisilanoxy)disilane	(278.2°) $n_D^{30}$ 1.4395	62
C <sub>15</sub> H <sub>20</sub> Si <sub>2</sub>	1 <i>H</i> -Trimethyl-1,2-diphenyldisilane	(86°–87°/0.05 mm) $n_D^{20}$ 1.5690	21

C <sub>15</sub> H <sub>24</sub> FeSi <sub>2</sub>	Pentamethyldisilanylferrocene	54.8°	80b
C <sub>16</sub> H <sub>20</sub> Br <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>p</i> -bromophenyl)tetramethyldisilane	81.5°–82.5°	57
C <sub>16</sub> H <sub>20</sub> Cl <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>p</i> -chlorophenyl)tetramethyldisilane	61°–62°	57
C <sub>16</sub> H <sub>20</sub> F <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>m</i> -fluorophenyl)tetramethyldisilane	40°–41°	57
		(122°–123°/0.7 mm)	
C <sub>16</sub> H <sub>22</sub> Si <sub>2</sub>	Tetramethyl-1,2-diphenyldisilane	(73°/0.01 mm)	85
C <sub>16</sub> H <sub>22</sub> Si <sub>2</sub>	Tetramethyl-1,1-diphenyldisilane	(98°–99°/0.23 mm)	57, 84
		$n_D^{20}$ 1.5660	
C <sub>16</sub> H <sub>22</sub> Si <sub>2</sub>	1 <i>H</i> ,2 <i>H</i> -1,2-Diethyldiphenyldisilane	(110°–111°/0.1 mm)	32, 41
		$n_D^{20}$ 1.5656	
C <sub>16</sub> H <sub>30</sub> Si <sub>2</sub>	Pentaethylphenyldisilane	(144°/3.5 mm)	81
		$n_D^{20}$ 1.5225	
C <sub>16</sub> H <sub>34</sub> Si <sub>4</sub>	<i>p</i> -Bis(pentamethyldisilanyl)benzene	80° (130°/4 mm)	81
C <sub>18</sub> H <sub>26</sub> Si <sub>2</sub>	Tetramethyl-1,2-di- <i>p</i> -tolylidisilane	70°–72°	85a
C <sub>18</sub> H <sub>26</sub> O <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>p</i> -methoxyphenyl)tetramethyldisilane	45°–46°	57
C <sub>18</sub> H <sub>42</sub> Si <sub>2</sub>	Hexa- <i>n</i> -propyldisilane	(128.5°–129°/1.5 mm)	26, 33
		$n_D^{20}$ 1.4721	
C <sub>20</sub> H <sub>22</sub> Si <sub>2</sub>	Tetramethyl-1,2-bis(phenylethynyl)disilane	76°–78°	48
C <sub>20</sub> H <sub>30</sub> Si <sub>2</sub>	Tetraethyl-1,2-diphenyldisilane	(190°–192°/3.5 mm)	81
		$n_D^{20}$ 1.5563	
C <sub>20</sub> H <sub>32</sub> N <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>p</i> -dimethylaminophenyl)tetramethyldisilane	150.5°–151.5°	57
C <sub>20</sub> H <sub>36</sub> FeSi <sub>4</sub>	1,1'-Bis(pentamethyldisilanyl)ferrocene	58.4°	80b
C <sub>20</sub> H <sub>50</sub> HgSi <sub>4</sub>	Bis(pentaethyldisilanyl)mercury	(180°–190°/1 mm)	83b
C <sub>21</sub> H <sub>24</sub> Si <sub>2</sub>	1,1,1-Trimethyltriphenyldisilane	108°–109°	41, 48, 86
		(218°–220°/11 mm)	
C <sub>21</sub> H <sub>24</sub> Si <sub>2</sub>	1,1,2-Trimethyltriphenyldisilane	(156°–157°/0.17 mm)	57
		$n_D^{20}$ 1.6027	
C <sub>22</sub> H <sub>34</sub> Si <sub>2</sub>	1,2-Diethyl-1,2-diphenyldi- <i>n</i> -propyldisilane	(265°–270°/100 mm)	34
C <sub>22</sub> H <sub>38</sub> Si <sub>4</sub>	1,2-Bis( <i>p</i> -trimethylsilylphenyl)tetramethyldisilane	111°–112°	57
C <sub>24</sub> H <sub>20</sub> Br <sub>2</sub> Si <sub>2</sub>	1,2-Dibromotetraphenyldisilane	154.5°–155.5°	42
C <sub>24</sub> H <sub>20</sub> Cl <sub>2</sub> Si <sub>2</sub>	1,2-Dichlorotetraphenyldisilane	114.5°–115°	42
C <sub>24</sub> H <sub>22</sub> Si <sub>2</sub>	1 <i>H</i> , 2 <i>H</i> -Tetraphenyldisilane	79°–80°	41, 87

TABLE I—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Disilanes (continued)</i>			
C <sub>24</sub> H <sub>22</sub> O <sub>2</sub> Si <sub>2</sub>	Tetraphenyldisilane-1,2-diol	138°–139°	42
C <sub>24</sub> H <sub>38</sub> Si <sub>2</sub>	1,2-Dibenzyl-1,2-diethyldi- <i>n</i> -propyldisilane	(244°–248°/20 mm)	34
C <sub>24</sub> H <sub>54</sub> Si <sub>2</sub>	Hexa- <i>n</i> -butyldisilane	(185.5°–190°/1.5 mm)	33
		<i>n</i> <sub>D</sub> <sup>20</sup> 1.4694	
C <sub>25</sub> H <sub>24</sub> Si <sub>2</sub>	1 <i>H</i> -2-Methyltetraphenyldisilane	71°–73°	88
C <sub>26</sub> H <sub>26</sub> Si <sub>2</sub>	1,1-Dimethyltetraphenyldisilane	81.5°–83°	85
C <sub>26</sub> H <sub>26</sub> Si <sub>2</sub>	1,2-Dimethyltetraphenyldisilane	141°–143°	41, 85
C <sub>28</sub> H <sub>28</sub> Si <sub>2</sub>	1,1,2,2-Tetraphenyl-1,2-disilacyclohexane	110°–111°	89
C <sub>29</sub> H <sub>30</sub> Si <sub>2</sub>	1,1,2,2-Tetraphenyl-1,2-disilacycloheptane	114.5°–115.5°	89
C <sub>30</sub> H <sub>25</sub> ClSi <sub>2</sub>	Chloropentaphenyldisilane	154°–155°	51
C <sub>30</sub> H <sub>66</sub> Si <sub>2</sub>	Hexaisoamyldisilane	(185.9°–186°/2 mm)	33
		<i>n</i> <sub>D</sub> <sup>20</sup> 1.4667	
C <sub>31</sub> H <sub>28</sub> Si <sub>2</sub>	Methylpentaphenyldisilane	147°–148°	84
C <sub>32</sub> H <sub>30</sub> Si <sub>2</sub>	Ethylpentaphenyldisilane	148°–149°	90
C <sub>34</sub> H <sub>34</sub> Si <sub>2</sub>	<i>n</i> -Butylpentaphenyldisilane	224°–226°	85a
C <sub>36</sub> H <sub>28</sub> Br <sub>2</sub> Si <sub>2</sub>	1,2-Bis( <i>p</i> -bromophenyl)tetraphenyldisilane	—	91
C <sub>36</sub> H <sub>30</sub> Si <sub>2</sub>	Hexaphenyldisilane	366°–370°	32, 41, 91, 92, 93
C <sub>36</sub> H <sub>66</sub> Si <sub>2</sub>	Hexacyclohexyldisilane	351°	94
C <sub>36</sub> H <sub>78</sub> Si <sub>2</sub>	Hexa- <i>n</i> -hexyldisilane	(235°–236°/0.5 mm)	33
		<i>n</i> <sub>D</sub> <sup>20</sup> 1.4691	
C <sub>38</sub> H <sub>34</sub> Si <sub>2</sub>	Tetraphenyl-1,2-di- <i>p</i> -tolylidisilane	251°–253°	41, 43
C <sub>42</sub> H <sub>42</sub> Si <sub>2</sub>	Hexabenzylidisilane	194°	27
C <sub>42</sub> H <sub>42</sub> Si <sub>2</sub>	Hexa- <i>p</i> -tolylidisilane	345°	26
C <sub>48</sub> H <sub>40</sub> Cl <sub>2</sub> OSi <sub>4</sub>	1,3-Bis(chlorodiphenylsila)tetraphenyldisiloxane	114°–116°	95

$C_{48}H_{40}Cl_2O_2Si_4$	1-(Chlorodiphenylsila)-3-(chlorodiphenylsiloxy)tetraphenyldisiloxane	104°–105°	95
$C_{48}H_{40}Cl_2O_2Si_4$	1,3-Bis(chlorodiphenylsiloxy)tetraphenyldisilane	148°–149°	95
$C_{48}H_{40}O_3Si_4$	Octaphenyl-1,3,5-trioxa-2,4,6,7-tetrasilacycloheptane	222°–223°, 229°–230°	95
$C_{50}H_{42}Si_2$	1,2-Bis(benzhydryl)tetraphenyldisilane	251°–252.5°	96
$C_{54}H_{54}O_4Si_4$	1,6-Di- <i>n</i> -propoxyoctaphenyl-2,5-dioxa-1,3,4,6-tetrasilahexane	106°–107°	95
$C_{66}H_{114}Si_2$	1,1,1-Tri- <i>n</i> -hexadecyltriphenyldisilane	(320°–325°/0.001 mm) $n_D^{20}$ 1.5142	97
$C_{72}H_{54}Si_2$	Hexakis(4-biphenyl)disilane	432°–434°	28
<i>Trisilanes</i>			
$C_6H_{18}Cl_2Si_3$	1,3-Dichlorohexamethyltrisilane	(82°–83°/11 mm) $n_D^{20}$ 1.4852	18, 56
$C_6H_{20}Si_3$	1 <i>H</i> ,3 <i>H</i> -Hexamethyltrisilane	–68° (54°/22 mm) $n_D^{20}$ 1.4658	54, 80a
$C_8H_{21}NSi_3$	Heptamethyltrisilanyl 1-cyanide	(36°–40°/0.4 mm)	66
$C_8H_{23}ClSi_3$	2-(Chloromethyl)heptamethyltrisilane	(108°–109°/23 mm) $n_D^{20}$ 1.4851	1
$C_8H_{24}Si_3$	Octamethyltrisilane	–46° (175°–176°) $n_D^{20}$ 1.4610	18, 43, 66
$C_{12}H_{24}Si_3$	2 <i>H</i> -Hexamethyl-2-phenyltrisilane	(75°–80°/0.55 mm) $n_D^{20}$ 1.5273	21
$C_{12}H_{28}Si_3$	1,3-Diisopropenylhexamethyltrisilane	(110°/15 mm) $n_D^{20}$ 1.4983	82
$C_{13}H_{26}Si_3$	Heptamethyl-2-phenyltrisilane	(111°/2.7 mm) $n_D^{20}$ 1.5260	57, 80a
$C_{18}H_{28}Si_3$	Hexamethyl-1,3-diphenyltrisilane	(120°–122°/0.15 mm) $n_D^{20}$ 1.5663	57
$C_{18}H_{28}Si_3$	Hexamethyl-2,2-diphenyltrisilane	(105.5°–106°/0.2 mm) $n_D^{20}$ 1.5736	46, 58
$C_{22}H_{28}Si_3$	Hexamethyl-1,3-bis(phenylethynyl)trisilane	(165°–167°/0.15 mm) $n_D^{20}$ 1.5895	48

TABLE I—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Trisilanes (continued)</i>			
C <sub>28</sub> H <sub>32</sub> Si <sub>3</sub>	1,2,2,3-Tetramethyltetraphenyltrisilane	62.5°–64°	57
C <sub>42</sub> H <sub>35</sub> ClSi <sub>3</sub>	1-Chloroheptaphenyltrisilane	160°–162°	48
C <sub>42</sub> H <sub>36</sub> Si <sub>3</sub>	1 <i>H</i> -Heptaphenyltrisilane	157°–158°	19, 53
C <sub>42</sub> H <sub>36</sub> OSi <sub>3</sub>	Heptaphenyltrisilan-1-ol	165°–166°	53
C <sub>48</sub> H <sub>40</sub> Si <sub>3</sub>	Octaphenyltrisilane	260°, 309°	19
C <sub>48</sub> H <sub>40</sub> Cl <sub>2</sub> OSi <sub>4</sub>	1-Chloro-3-(chlorodiphenylsiloxy)hexaphenyltrisilane	169°–170°	95
C <sub>48</sub> H <sub>40</sub> O <sub>2</sub> Si <sub>4</sub>	Octaphenyl-1,3-dioxa-2,4,5,6-tetrasilacyclohexane	245°–246°, 256°–257°	95
<i>Tetrasilanes</i>			
C <sub>8</sub> H <sub>24</sub> Cl <sub>2</sub> Si <sub>4</sub>	1,4-Dichlorooctamethyltetrasilane	(76°–78°/1.0 mm) $n_D^{20}$ 1.5035	56, 80a
C <sub>8</sub> H <sub>26</sub> Si <sub>4</sub>	1 <i>H</i> ,4 <i>H</i> -Octamethyltetrasilane	(68°–70°/1 mm) $n_D^{20}$ 1.4915	23, 54, 80a
C <sub>10</sub> H <sub>27</sub> NSi <sub>4</sub>	Nonamethyltetrasilanyl 1-cyanide	(65°–75°/0.4 mm)	66
C <sub>10</sub> H <sub>30</sub> Si <sub>4</sub>	Decamethyltetrasilane	–12° (109°/15 mm) $n_D^{20}$ 1.4878	18, 43, 56, 66
C <sub>12</sub> H <sub>30</sub> Si <sub>4</sub>	Octamethyl-1,4-divinyltetrasilane	(97°/1.5 mm) $n_D^{20}$ 1.5097	57
C <sub>12</sub> H <sub>32</sub> Si <sub>4</sub>	1,1,2,2,3,3,4,4,5,5-Decamethyl-1,2,3,4-tetrasilacyclohexane	44°–45°	68
C <sub>15</sub> H <sub>32</sub> Si <sub>4</sub>	Tris(trimethylsilyl)phenylsilane	Waxy solid sublimes (140°/0.05 mm)	21
C <sub>20</sub> H <sub>34</sub> Si <sub>4</sub>	Octamethyl-1,4-diphenyltetrasilane	59°–61°	56, 80a
C <sub>20</sub> H <sub>50</sub> Si <sub>4</sub>	Decaethyltetrasilane	(164°–170°/1 mm)	44
C <sub>24</sub> H <sub>34</sub> Si <sub>4</sub>	Tris(dimethylphenylsilyl)silane	68°–69.5°	20

$C_{24}H_{34}Si_4$	Octamethyl-1,4-bis(phenylethynyl)tetrasilane	(158°–161°/0.025 mm) $n_D^{20}$ 1.5943	48
$C_{30}H_{38}Si_4$	Hexamethyl-2,2,3,3-tetraphenyltetrasilane	265°–267°	21, 46
$C_{40}H_{42}Si_4$	2,2,3,3-Tetramethylhexaphenyltetrasilane	209°–210°	48
$C_{48}H_{42}Si_4$	1 <i>H</i> , 4 <i>H</i> -Octaphenyltetrasilane	161°–162°	53
$C_{51}H_{48}OSi_4$	1 <i>H</i> -4- <i>n</i> -Propoxyoctaphenyltetrasilane	140°–141°	95
$C_{52}H_{46}O_4Si_4$	1,4-Diacetoxyoctaphenyltetrasilane	233°–235°	55
$C_{54}H_{46}Si_4$	Tris(triphenylsilyl)silane	206°–209°	19
$C_{55}H_{48}Si_4$	1 <i>H</i> -4- <i>p</i> -Tolyloctaphenyltetrasilane	185°–187°	98
$C_{60}H_{50}Si_4$	Decaphenyltetrasilane	350°–352°	53, 54
$C_{64}H_{50}Si_4$	Octaphenyl-1,4-bis(phenylethynyl)tetrasilane	187°–189°	98
<i>Pentasilanes</i>			
$C_8H_{28}Si_5$	Tetrakis(dimethylsilyl)silane	(126°–130°/19 mm) $n_D^{20}$ 1.5175	23
$C_{10}H_{32}Si_5$	1 <i>H</i> ,5 <i>H</i> -Decamethylpentasilane		54
$C_{12}H_{33}NSi_5$	Undecamethylpentasilanyl 1-cyanide	(67.5°–71°/0.2 mm)	66
$C_{12}H_{36}Si_5$	Tetrakis(trimethylsilyl)silane	261°–263° (sublimes)	22
$C_{12}H_{36}Si_5$	Dodecamethylpentasilane	–34° (135°–136°/13 mm) $n_D^{20}$ 1.5060	18, 66
$C_{22}H_{40}Si_5$	Decamethyl-1,5-diphenylpentasilane	61°–63.5°	57
$C_{32}H_{44}Si_5$	Octamethyl-2,2,4,4-tetraphenylpentasilane	97°–97.5°	46
$C_{42}H_{48}Si_5$	2,2,3,3,4,4-Hexamethylhexaphenylpentasilane	185°–186.5°	48
$C_{50}H_{46}Si_5$	1,1-Dimethyloctaphenylcyclopentasilane	315°–317°	61
$C_{60}H_{50}OSi_5$	Decaphenyloxacyclohexasilane	425°–426°	99
$C_{63}H_{56}Si_5$	1,1,2,2,3,3,4,4,5,5-Decaphenyl-1,2,3,4,5-pentasilacyclooctane	290°–291°	59
$C_{64}H_{60}O_2Si_5$	1,5-Bis( $\beta$ -hydroxyethyl)decaphenylpentasilane	167°–169°	20
$C_{66}H_{60}O_2Si_5$	1,5-Bis(allyloxy)decaphenylpentasilane	176°–177°	95
<i>Hexasilanes</i>			
$C_{12}H_{36}Si_6$	Dodecamethylcyclohexasilane	250°–252° (sublimes)	50, 100



TABLE 1—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Hexasilanes (continued)</i>			
C <sub>12</sub> H <sub>36</sub> Cl <sub>2</sub> Si <sub>6</sub>	1,6-Dichlorododecamethylhexasilane	45°–46.5° (143°–144°/0.02 mm)	23, 56
C <sub>12</sub> H <sub>36</sub> I <sub>2</sub> Si <sub>6</sub>	1,6-Diiodododecamethylhexasilane	(185°/2 mm)	50
C <sub>12</sub> H <sub>36</sub> OSi <sub>6</sub>	Dodecamethyloxacycloheptasilane	144°–147°	99
C <sub>12</sub> H <sub>38</sub> Si <sub>6</sub>	1 <i>H</i> ,6 <i>H</i> -Dodecamethylhexasilane	(103°/0.12 mm) $n_D^{20}$ 1.5251	23
C <sub>14</sub> H <sub>39</sub> NSi <sub>6</sub>	Tridecamethylhexasilanyl 1-cyanide	—	66
C <sub>14</sub> H <sub>42</sub> Si <sub>6</sub>	Tetradecamethylhexasilane	28°–29° (165°/10 mm) $n_D^{20}$ 1.5139	18, 56
C <sub>24</sub> H <sub>46</sub> Si <sub>6</sub>	Dodecamethyl-1,6-diphenylhexasilane	86°–87°	56
C <sub>28</sub> H <sub>46</sub> Si <sub>6</sub>	Dodecamethyl-1,6-bis(phenylethynyl)hexasilane	(180°–181°/0.015 mm) $n_D^{20}$ 1.5910	48
C <sub>28</sub> H <sub>56</sub> N <sub>2</sub> Si <sub>6</sub>	1,6-Bis( <i>p</i> -dimethylaminophenyl)dodecamethylhexasilane	148.5°–149.5°	57
C <sub>44</sub> H <sub>54</sub> Si <sub>6</sub>	Octamethyl-1,1,1,6,6,6-hexaphenylhexasilane	180°–182°	20
C <sub>62</sub> H <sub>56</sub> Si <sub>6</sub>	1,1-Dimethyldecaphenylcyclohexasilane	472°–476°	61
C <sub>72</sub> H <sub>60</sub> Br <sub>2</sub> Si <sub>6</sub>	1,6-Dibromododecaphenylhexasilane	230°–232°	48
C <sub>72</sub> H <sub>60</sub> Cl <sub>2</sub> Si <sub>6</sub>	1,6-Dichlorododecaphenylhexasilane	239°–241°	47
C <sub>72</sub> H <sub>62</sub> Si <sub>6</sub>	1 <i>H</i> ,6 <i>H</i> -Dodecaphenylhexasilane	185°–187°	47
C <sub>74</sub> H <sub>66</sub> Si <sub>6</sub>	1,6-Dimethyldodecaphenylhexasilane	209°–211°	47
C <sub>84</sub> H <sub>70</sub> Si <sub>6</sub>	Tetradecaphenylhexasilane	330°–332°	48
<i>Heptasilane</i>			
C <sub>16</sub> H <sub>48</sub> Si <sub>7</sub>	Hexadecamethylheptasilane	19°–20° (194°/16 mm) $n_D^{20}$ 1.5264	18

*Octasilanes*

$C_{18}H_{48}N_2Si_8$	Hexadecamethyloctasilanyl 1,8-dicyanide	—	66
$C_{18}H_{51}NSi_8$	Heptadecamethyloctasilanyl 1-cyanide	—	66
$C_{18}H_{54}Si_8$	Octadecamethyloctasilane	60°–61° (194°–198°/3 mm)	1
$C_{48}H_{88}Si_8$	Dodecamethyl-1,1,1,8,8,8-hexaphenyloctasilane	154°–156°	20

*Decasilanes*

$C_{22}H_{66}Si_{10}$	Docosamethyldecasilane	113°–114° (244°/13 mm)	1
$C_{72}H_{86}Si_{10}$	Dodecamethyl-1,1,1,2,2,9,9,10,10,10-decaphenyldecasilane	215°–218°	20

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<sup>a</sup> Boiling point values are given in parentheses.

## C. Physical Properties

### 1. Thermal Stability

The lower alkyl polysilanes are generally liquids, while the perarylated derivatives are solids. Exceptions are noted with alkylated derivatives, and octadecamethyloctasilane and docosamethyldecasilane are solids melting at 60°–61° C and 113°–114° C, respectively (1). Hexacyclohexyldisilane (94) is a high-melting solid, while dodecamethylcyclohexasilane (m.p. 250°–252° C, see 14) and tetrakis(trimethylsilyl)silane (m.p. 261°–263° C, see 22) are high-melting and easily sublimable solids. Mixed aralkyl polysilanes may favor either parent series. Thus, 1,2-diethyl-1,2-diphenyldi-*n*-propyldisilane boils without decomposition at 268° C (100 mm, 34), whereas octamethyl-1,4-diphenyltetrasilane is a solid, m.p. 60°–62° C (56).

Apparently all organopolysilanes are stable to spontaneous decomposition, and the majority of them melt without decomposition. In the cyclosilane series, octaphenylcyclotetrasilane (14), octa-*p*-tolylcyclotetrasilane (14), decaphenylcyclopentasilane (14, 58), and dodecaphenylcyclohexasilane (14, 58, 101) all decompose to some extent at their melting points. Although dodecamethylcyclohexasilane (14) appears to be stable toward decomposition, it is reported (102) to undergo an irreversible change in crystalline form when heated to temperatures greater than 74° C.

Hexamethyl-2*H*-2-phenyltrisilane has been observed to decompose slowly in air and to inflame when heated in the presence of air (21).

### 2. Spectral

a. *Infrared (IR) and Raman (R)*. The spectral data for hexaethyldisilane (IR, R, 103), hexamethyldisilane (IR, R, 2, 104), fluoropentamethyldisilane (IR, R, 2), 1,2-difluorotetramethyldisilane (2), 1,2-dichlorotetramethyldisilane (IR, R in gas, liquid, and solid state, 105), hexaphenyldisilane (IR, 93), hexacyclohexyldisilane (IR, 94), vinylpentamethyldisilane (IR, 106), allylpentamethyldisilane (IR, 106), but-3-ene-1-ylpentamethyldisilane (IR, 106), 1*H*-pentamethyldisilane (IR, R, 107), bromopentamethyldisilane (IR, R, 107), pentamethyldisilanol (IR, R, 107), and bis(pentamethyldisilanyl) ether (IR, R, 107) have been reported.

Little infrared work has been reported concerning the higher polysilanes. A study of the infrared spectra of  $\alpha,\omega$ -dihaloperphenylated polysilanes,  $\text{Cl}[(\text{C}_6\text{H}_5)_2\text{Si}]_n\text{Cl}$ , in the 400–800  $\text{cm}^{-1}$  region has been carried out (95), and a dependence of the band frequencies on chain length is indicated.

A study of the infrared spectra of octaphenylcyclotetrasilane, decaphenylcyclopentasilane, dodecaphenylcyclohexasilane, and 1,5-di-*n*-butyldeca-phenylpentasilane has been carried out (58). While the spectra of the three cyclosilanes are almost identical in the 5000–700  $\text{cm}^{-1}$  range, significant differences are evident in the 700–200  $\text{cm}^{-1}$  region. The infrared and Raman spectra of octamethyltrisilane (107), decamethyltetrasilane (107), dodecamethylpentasilane (107), and dodecamethylcyclohexasilane (107), and a number of methylated polysilanyl cyanides (108) have been determined.

Some interesting observations can be made with the perphenylated derivatives. For the series  $(\text{C}_6\text{H}_5)_4\text{M}$  (where M is a Group IVB element) an absorption due to the  $\text{C}_6\text{H}_5\text{—M}$  linkage appears at 9.04 (M = Si), 9.18 (M = Ge), 9.30 (M = Sn), and 9.43  $\mu$  (M = Pb) (109). These compounds show a linear relationship between absorption frequency and the square of the electronegativity of the central atom. Since the above relationship holds regardless of additional groups attached to the M atom, it was suggested (93) that the frequency is not a function of the substituent group, but rather of the electronegativity of the element directly attached to the phenyl group. Recent observations on the infrared spectra of polysilanes indicate that this latter suggestion does not necessarily hold true in all cases. As one goes from  $(\text{C}_6\text{H}_5)_4\text{Si}$  to  $(\text{C}_6\text{H}_5)_6\text{Si}_2$ , very slight changes are observed in the frequency of the 9.04  $\mu$  band, and compounds of these types normally show  $[\text{C}_6\text{H}_5]\text{—Si}$  absorption bands in the 8.95–9.10  $\mu$  region (110). Recently, however, a number of tetrasilane derivatives have been found (111) to show significant shifts in the position of this band, and observed values of 9.10 and 9.15  $\mu$  seem to indicate a dependence of this frequency on the nature of the polysilane chain. For example, the frequency of this band appears to be dependent on the degree of Si substitution. The shifts observed as one proceeds from a “primary” to a “tertiary” silyl-substituted silicon atom are shown on p. 26.<sup>3</sup>

A similar correlation is found in the observed frequency of the Si—H bond upon going from a “primary” to a “tertiary” silicon atom (21, 89). This effect is directly opposite to that observed (112) when electronegative groups are attached to silicon bearing a hydrogen atom, and the shifts to lower stretching frequencies indicate a weakening of the Si—H bond (presumably caused by a reduction of the electronegativity of the most highly substituted

<sup>3</sup> The terms “primary,” “secondary,” etc., designate the degree of silyl substitution of a specific silicon atom, analogous to the use of these terms in carbon chemistry.

	<i>Band position (<math>\mu</math>) (21, 89)</i>
$\begin{array}{c} (\text{CH}_3)_3\text{Si}-\text{Si}(\text{C}_6\text{H}_5)_3 \\   \\ \text{C}_6\text{H}_5 \end{array}$	9.09
$\begin{array}{c} (\text{CH}_3)_3\text{Si}-\text{Si}-\text{Si}(\text{CH}_3)_3 \\   \\ \text{C}_6\text{H}_5 \\   \\ \text{C}_6\text{H}_5 \end{array}$	9.16
$\begin{array}{c} (\text{CH}_3)_3\text{Si}-\text{Si}-\text{Si}(\text{CH}_3)_3 \\   \\ \text{Si}(\text{CH}_3)_3 \end{array}$	9.23

silicon atom) as one goes from a "primary" to a "tertiary" silicon atom. An opposite effect appears to have been observed for the Si—H group in isotetrasilane (113). While the compounds examined have been few in

	<i>Band position (<math>\mu</math>)</i>
$\begin{array}{c} (\text{CH}_3)_3\text{Si}-\text{Si}(\text{C}_6\text{H}_5)_2\text{H} \\   \\ \text{C}_6\text{H}_5 \end{array}$	4.77
$\begin{array}{c} (\text{CH}_3)_3\text{Si}-\text{Si}-\text{Si}(\text{CH}_3)_3 \\   \\ \text{H} \end{array}$	4.83
$\begin{array}{c} \text{C}_6\text{H}_5(\text{CH}_3)_2\text{Si}-\text{Si}-\text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5 \\   \\ \text{Si}(\text{CH}_3)_2\text{C}_6\text{H}_5 \end{array}$	4.88

number, there is indication that information concerning the electronegativity of these branched silyl groups can be approximated. For example, the value of 9.23  $\mu$  obtained for the  $\text{C}_6\text{H}_5\text{—Si}$  linkage in tris(trimethylsilyl)phenylsilane is comparable to that obtained for the  $\text{C}_6\text{H}_5\text{—Ge}$  linkage in hexaphenyldigermane (9.21  $\mu$ ), indicating a similarity between the electronegativity of the  $[(\text{CH}_3)_3\text{Si}]_3\text{Si}$  group and that of germanium. Likewise, the value obtained for the Si—H in tris(dimethylphenylsilyl)silane (4.88  $\mu$ ) is comparable to that obtained with triphenylgermane ( $\text{GeH} = 4.90 \mu$ ). While such studies are in their infancy, hopefully correlations of this type will provide useful information concerning the reactivity of linear, cyclic, and branched polysilanes.

b. *Ultraviolet*. The color of certain compounds containing the Si—Si bond (silicon subhalides, siloxanes) has been attributed to a hybridization of the free orbitals of the silicon atoms which in the Si—Si bond causes a strengthening of the bond and a configuration with electron mobility (114–116). While the ultraviolet properties of numerous monosilane derivatives

have been previously reported (14, 92), it is only recently that the spectral properties of polysilanes have been examined. Hague and Prince (92, 116a) have reported that Group IVB compounds of the type  $(C_6H_5)_3MM(C_6H_5)_3$  ( $M = Si, Ge, Sn, \text{ and } Pb$ ) show ultraviolet maxima in the 239–248  $m\mu$  region [ $\epsilon = 30,400\text{--}33,900$ ]. Thus, hexaphenyldisilane has  $\lambda_{\max} = 246.5 m\mu$  [ $\epsilon = 32,600$ ]. These spectral properties suggested an intense interaction between phenyl groups on different  $M$  atoms through the  $M\text{--}M$  bond. Further, this unusual type of conjugation was considered to occur through overlap of  $p\pi$  orbitals with suitable vacant  $d$  orbitals on the  $M$  atom (i.e.,  $p\pi\text{--}d\pi$  and  $d\pi\text{--}d\pi$  interactions). Also, compounds of the type  $[(C_6H_5)_2Si]_n$  (where  $n = 4, 5, 6$ ) have been reported (117) to exhibit intense ultraviolet maxima in the 250–285  $m\mu$  region. An examination (118) of a homologous series of  $\alpha,\omega$ -diphenylpermethylated polysilanes,  $C_6H_5\text{--}[(CH_3)_2Si]_n\text{--}C_6H_5$  (where  $n = 2$  to 6) gave maxima in the 236 to 265  $m\mu$  region ( $\epsilon = 18,200$  to 30,500). A recent investigation (119) of the ultraviolet properties of a family of permethylated linear polysilanes  $CH_3[(CH_3)_2Si]_nCH_3$  implies that the polysilane chain itself absorbs ultraviolet radiation without the presence of phenyl groups.

While dodecamethylcyclohexasilane has been reported (49) to have  $\lambda_{\max} = 280 m\mu$ , we find that analytically pure samples of this material show  $\lambda_{\max} = 231 m\mu$  (57, 89).

All the compounds of the series hexamethyldisilane to hexaphenyldisilane (a family of disilanes which has only phenyl and methyl groups attached to silicon) have been examined (119) and show maxima in the 199.5–246.5  $m\mu$  region ( $\epsilon = 7230$  to 32,600). The most pronounced increase in the  $\lambda_{\max}$  is observed when one methyl group is replaced by a phenyl group to give pentamethylphenyldisilane ( $\lambda_{\max} = 230.5 m\mu$ ,  $\epsilon = 11,204$ ). At the present time, 1,1,9,9-tetramethylhexadecaphenylnonasilane (120) has given the most dramatic shifts in  $\lambda_{\max}$  with values of 335 and 260 [shoulder]  $m\mu$  being obtained (57, 89).

Present studies on the ultraviolet properties of polysilanes have led to the following observations (118, 119, 119a):

(a) Phenyl-containing monosilanes exhibit only the benzenoid fine structure of B bands having low molar absorptivities (2, 92).

(b) With polysilanes, intense absorption maxima are observed and the  $\lambda_{\max}$  increases with increasing chain length. In some instances a regular increase is observed.

(c) The  $\epsilon$  values also increase with increasing chain length. These compounds appear to obey Beer's Law.

(d) Substituents such as  $C_6H_5-$  and  $CH_2=CH-$  cause an increase in  $\lambda_{max}$ , while  $Cl-$ ,  $HO-$ , and  $H-$  appear to have little effect on the band position (95, 119).

(e) Cyclic and branched polysilanes absorb at lower wavelengths than their corresponding open-chain analogs (57, 89).

From the foregoing discussion it appears that the unique spectral properties of polysilanes are due to the Si—Si bond acting as a chromophore, probably through the use of vacant  $d$  orbitals of the silicon atom ( $d\pi-d\pi$  double-bond character). While these spectral properties promise to be extremely useful in a study of numerous organic and inorganic polysilanes, further studies are necessary to determine the precise nature of the electronic excitations involved.

c. *Nuclear Magnetic Resonance (NMR)*. A study of the NMR spectra of the series  $[CH_3]_3M-M[CH_3]_3$  (where  $M = C, Si, Ge, Sn$ ) has been carried out (79, 80). The proton shielding of the methyl groups bound to silicon ( $9.963 \pm 0.002\tau$ ) was found to be greater than in the carbon analog ( $9.130 \pm 0.007\tau$ ), but slightly less than that of tetramethylsilane ( $10.00\tau$ ). The NMR spectra of dodecamethylcyclohexasilane (50), tetradecamethylhexasilane (50), heptamethyltrisilanyl 1-cyanide (66) and tetrakis(trimethylsilyl)silane (22) have been reported, and internal Si— $CH_3$  groups are deshielded with respect to the terminal Si— $CH_3$  groups.

The most extensive use of NMR in the field of polysilanes has been for the determination of structure by comparison of area ratios. Accurate information on the length of polysilane chains has been obtained in numerous cases (for example, see refs. 14, 55, 58, 59, 61, 66, and 120). Recent results, however, suggest that NMR may provide useful information concerning the character of the Si—Si bond. For example, an increase in shielding occurs on going from the Si—Si—H group to the  $(Si)_3Si-H$  group. Thus, as one proceeds from a "primary" to a "tertiary" silicon atom, the shielding of the protons attached to this silicon atom increases. These results can be explained in terms of a reduction in electronegativity of the most highly substituted silicon atom. A similar observation has been reported (113) for isotetrasilane (Si— $H_3$ ,  $6.58\tau$ ;  $Si-H$ ,  $7.07\tau$ ). With monosilanes containing electronegative substituents, deshielding effects are observed for Si—H protons in the NMR spectra, together with a shift to higher stretching frequencies in the infrared spectra (89, 112).

	<i>Si—H band position (<math>\tau</math>) (57, 89)</i>
$\begin{array}{c} \text{(CH}_3\text{)}_3\text{Si—Si(C}_6\text{H}_5\text{)}_2\text{H} \\   \\ \text{C}_6\text{H}_5 \end{array}$	5.20
$\begin{array}{c} \text{(CH}_3\text{)}_3\text{Si—Si—Si(CH}_3\text{)}_3 \\   \\ \text{H} \end{array}$	6.40
$\begin{array}{c} \text{C}_6\text{H}_5\text{(CH}_3\text{)}_2\text{Si—Si—Si(CH}_3\text{)}_2\text{C}_6\text{H}_5 \\   \\ \text{Si(CH}_3\text{)}_2\text{C}_6\text{H}_5 \end{array}$	7.32

Finally, a study of the NMR spectra of various disilanes of the type  $\text{H}_3\text{SiSiH}_2\text{X}$  (121), and also of a number of substituted methylated polysilanes (108), suggests that the Si—Si bonds in these compounds contain some  $d\pi-d\pi$  double-bond character. This latter observation is compatible with other spectral and chemical (81, 134) evidence reported for polysilanes.

### 3. Bond Length and Energy

Generally, bonds formed by silicon to other elements are stronger than those formed by carbon (2). Also, chemical evidence has been cited (3) which suggests that in some cases, Si—Si bonds are more thermally stable than the corresponding C—C bonds. For a number of years, only a limited amount of thermochemical data for the Si—Si bond was available, and this information indicated that this bond is considerably weaker than the C—C bond. Thus, a value of  $46.4 \text{ kcal mole}^{-1}$  has been cited (122) as the thermochemical bond energy [ $E(\text{Si—Si})$ ] for disilane, and the activation energy for the pyrolysis of disilane has been taken to imply a bond dissociation energy [ $D(\text{Si—Si})$ ] of  $51 \text{ kcal mole}^{-1}$ . Recently, however, the dissociation energy of the Si—Si bond (in  $\text{H}_3\text{SiSiH}_3$ ) has been determined (123) by electron impact as  $81.3 \text{ kcal mole}^{-1}$ , comparable to the dissociation energy of the C—C bond in ethane ( $83 \text{ kcal mole}^{-1}$ ). These results agree favorably with the value of  $83.7 \text{ kcal mole}^{-1}$  calculated (124, 124a) for the bond energy of disilane using the appearance potentials obtained from the mass spectrum. Also, hexamethyldisilane has been studied by electron impact and a value of  $81 \text{ kcal mole}^{-1}$  was found for the bond dissociation energy (125).

In the Si—Si bond, both atoms have equal electronegativity and the ionic character of this bond should be equal to zero. The bond energy considered above is that necessary to break the Si—Si bond in a homolytic fashion, and therefore gives an inaccurate prediction of the ease of heterolytic fission of this bond. Indeed, most reactions of the Si—Si bond are ionic



in nature. With regard to the chemistry of the Si—Si bond (as well as that of other bonds), the rate of breaking (or reaction) will be dependent on a combination of factors such as the reaction mechanism, steric factors, and inductive effects (3).

A study of the molecular structure of disilane, hexachlorodisilane, and hexamethyldisilane has been carried out (2) with the aid of electron diffraction, and the Si—Si bond lengths obtained ( $2.32 \pm 0.03$ ,  $2.32 \pm 0.06$ , and  $2.34 \pm 0.10$  Å, respectively) are roughly the same as that in elementary silicon. No information is available on the bond lengths of higher organopolysilanes.

The force constant of the Si—Si bond has been calculated as  $1.3 \times 10^5$  dynes  $\text{cm}^{-1}$ ; however, it is believed that this value is probably in error (104). The dipole moments of several aromatic disilanes have been reported (2) which allowed one to calculate an aryl—Si—aryl valence angle of  $115^\circ$ . The dipole moment of 1,2-dichlorotetramethyldisilane was found (105) to be 1.75 debye in carbon tetrachloride and 1.35 debye in benzene. On the basis of the dipole moments, the infrared and the Raman spectra (in the gas, liquid, and solid state), information on the rotation about the Si—Si axis in 1,2-dichlorotetramethyldisilane was obtained. In the solid state, the chlorine atoms assume the *trans* position, whereas in the liquid and gas state the molecule exerts torsional oscillations about the Si—Si axis to a certain extent. The phase transformations of hexamethyldisilane were studied by NMR (80) and thermodynamically by means of differential thermal analysis (25). From such studies it appears that at higher temperatures rotations about both the Si—Si and Si—CH<sub>3</sub> axes occur in combination with the overall molecular rotation about the molecular axis, whereas at lower temperatures all movements are hindered except for the Si—CH<sub>3</sub> axial rotation.

Although no information on the dipole moments of higher polysilanes has been reported, such studies are currently in progress (126).

From an examination of this section on physical properties it is immediately apparent that relatively few studies on the character of the Si—Si bond using physicochemical techniques have been carried out.

#### D. Chemical Properties

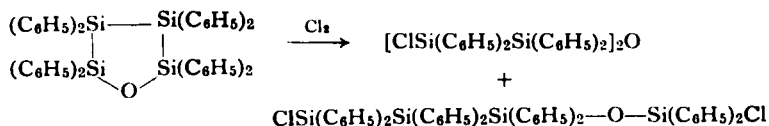
As we have previously remarked, the majority of the studies in the field of polysilanes have been, until recently, confined to the disilane derivatives.

Although the chemistry of the organic substituted disilanes has been recently reviewed (2), this section will briefly discuss their chemistry as it bears on the reactions of the higher polysilanes, followed by a consideration of the reactions of these latter compounds. In addition, reactions of the disilanes reported subsequent to this review (2) will be included. In general, we will consider first a particular facet of the chemistry of the disilanes, followed immediately by a discussion of the related reactions of the higher polysilanes.

### 1. Cleavage of the Silicon-Silicon Bond

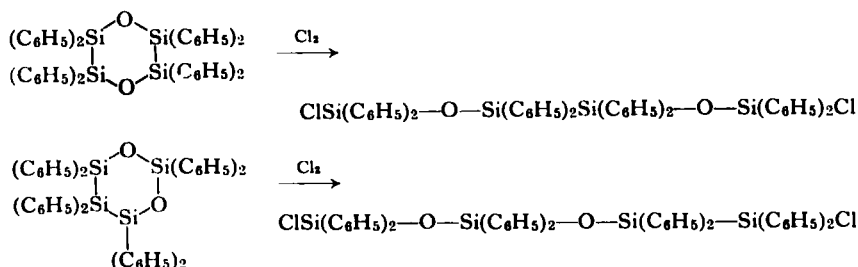
a. *Electrophilic and Oxidative.* The cleavage of the Si—Si bond with halogens has been the subject of numerous investigations (2, 14). The ease of cleavage is dependent on the halogen employed and on the substituents on silicon. Thus, hexaaryldisilanes are quite resistant to cleavage by halogens, while hexaalkyldisilanes are considerably more reactive. From a study of the reaction kinetics of the cleavage of various alkylidisilanes it was suggested that: (a) The first step in the reaction is the formation of addition products as the result of the attack of halogen molecules on the Si—Si bond. (b) The substitution of alkyl groups by halogen on the disilane linkage greatly reduces the rate of cleavage. (c) The relative reactivity of halogens with a given Si—Si bond appears to be  $\text{Cl}_2 > \text{Br}_2 > \text{I}_2$  (127).

In the case of higher polysilanes, similar cleavage reactions have been observed; however, in view of the presence of additional Si—Si bonds, reaction control is usually necessary to obtain the desired products. Thus, in the perphenylated cyclosilane series, octaphenylcyclotetrasilane (14) and decaphenylcyclopentasilane (14, 58) have been reported to react with halogens, and the order of halogen reactivity appears to parallel that observed with the hexaalkyldisilanes. On the other hand, dodecaphenylcyclohexasilane (14, 101) does not react with bromine or iodine and reacts with chlorine only under forced conditions. With dodecamethylcyclohexasilane, cleavage with chlorine (20), bromine (128), and iodine (50) has been observed.

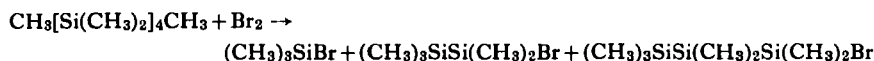


The chlorination of octaphenylloxacyclopentasilane gives two dichloro products resulting from both symmetrical and unsymmetrical Si—Si bond

cleavage (95). The cyclic siloxanes resulting from hydrolysis of the above linear dichloro compounds have also been cleaved by chlorine (95).

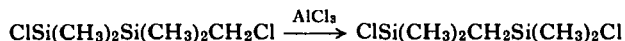


Cleavage of linear permethylated polysilanes with bromine has been reported (76). In addition to its synthetic value, this reaction can be used for the determination of the number of Si—Si bonds present (76, 129).



Octaphenylcyclotetrasilane is readily cleaved by hydrogen halides (HCl, HBr, and HI), inorganic halides, and a variety of halogenated hydrocarbons (14). Decaphenylcyclopentasilane reacts with some of these reagents (for example, phosphorus pentachloride, *sym*-tetrachloroethane); however, more vigorous reaction conditions are necessary. Dodecaphenylcyclohexasilane is even more inert toward these reagents (14). Dodecamethylcyclohexasilane reacts with mercuric chloride and *sym*-tetrachloroethane. While no reactions have been reported with hydrogen halides and dodecamethylcyclohexasilane, such investigations are in progress (95).

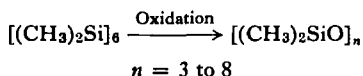
The reaction of hexaethyldisilane with aluminum chloride leads to the formation of silicon and tetraethylsilane (44). With 1-chloro-2(chloromethyl)tetramethyldisilane and aluminum chloride, isomerization to 1,3-dichloro-1,1,3,3-tetramethyldisilmethylene occurs, while chloromethylpentamethyldisilane gives chloropentamethyldisilmethylene (64).



Similar intramolecular isomerizations have been observed upon high-temperature pyrolysis of hexamethyldisilane (130) in a quartz tube, or by treatment of isopropenylpentamethyldisilane (82), 1,2-diisopropenyltetramethyldisilane (82), and 1,3-diisopropenylhexamethyltrisilane (82) with concentrated sulfuric acid.

Hexaaryldisilanes show no tendency to dissociate into radicals (2, 6), and no reactions occur with oxygen or oxidizing agents such as lead tetraacetate and selenium dioxide (2, 6, 14). In the cyclosilane series, octaphenylcyclotetrasilane is readily oxidized by oxygen and a variety of oxidizing agents (14). While reaction can be effected readily with nitrobenzene, ozone, and benzaldehyde, and slowly by benzyl alcohol, acetophenone, paraldehyde, and amyl nitrite, octaphenylcyclotetrasilane appears to be stable to aqueous oxidizing agents such as potassium permanganate and potassium dichromate. With the latter reagents, the lack of reactivity may be due to the insolubility of the cyclosilane in aqueous media.

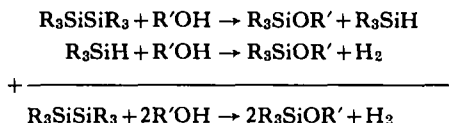
The reaction of dodecamethylcyclohexasilane with potassium permanganate, chromic oxide, and potassium dichromate in acetic acid gives a series of homologous cyclic siloxanes (20). Nitrobenzene and hydrogen peroxide (30%) in either formic acid or *tert*-butyl alcohol were found to be less effective oxidizing agents.



Recently, the cleavage of organodisilanes with metallic salts have been reported (133a). Similar cleavage reactions have been previously observed with octaphenylcyclotetrasilane (14).

Following the synthesis of several ferrocenyldisilanes, the first examples of acid cleavage of the Si—Si bond under mild conditions have been observed (80b).

b. *Nucleophilic and Reductive Cleavage.* Cleavage of the Si—Si bond in many disilanes can be achieved through the use of aqueous piperidine, and alkali in hexanol (2, 6, 14). The Si—Si bonds of hexaalkyldisilanes are resistant to alcoholic alkali and wet piperidine (2). This type of cleavage proceeds with the evolution of an equivalent of hydrogen for each Si—Si bond present, and constitutes the basis for the quantitative determination of the number of such bonds. The use of this technique was first reported by



Martin (131) and thereafter by Kipping (132), who described the advantageous use of moist piperidine. This procedure was refined and extended to the estimation of the Si—H group and finally to the determination, in some

cases, of the Si—Si bond in the presence of Si—H groups (42). The results are expressed in terms of a "hydrogen value" which is defined as the number of milliliters of gas (at STP) liberated per gram of compound. While octaphenylcyclotetrasilane and decaphenylcyclopentasilane give facile reactions with moist piperidine, dodecaphenylcyclohexasilane and dodecamethylcyclohexasilane do not react to an appreciable extent (6, 14, 88, 133). In the latter case reaction can be achieved with alkali in hexanol (102).

An extensive amount of research has been devoted to the cleavage of the Si—Si bond by metals and organometallics, and extensive coverage of these cleavages can be found in several recent reviews (2, 4, 5, 14, 140). Organic-substituted disilanes containing aryl groups can be cleaved by alkali metals in certain ethereal and amine solvents and in liquid ammonia. Presently, the method of choice for such cleavage reactions appears to be the cleavage of a disilane with lithium in tetrahydrofuran. Solutions of silylmetallics obtained in this manner are quite stable and easy to handle.

The cleavage of higher polysilanes with lithium (in tetrahydrofuran) has also been studied; however, in these cases mixtures of silyllithium reagents are obtained (5). Cleavage of octaphenyltrisilane gave a mixture of pentaphenyldisilanyl lithium and triphenylsilyllithium, whereas decaphenyltetrasilane gave a mixture of triphenylsilyllithium, pentaphenyldisilanyl lithium, and heptaphenyltrisilanyl lithium (5). The lithium cleavage of mixed

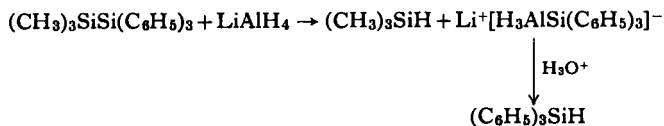


aralkyl polysilanes has also been observed (46). The cleavage of octamethyltrisilane and decamethyltetrasilane with sodium-potassium alloy (in tetrahydrofuran) has been reported (134). Derivatization of the resulting silylmetallic species with chlorotrimethylsilane gave a variety of linear and cyclic permethylated polysilanes. The metal cleavage of cyclosilanes has also been studied quite extensively (14, 21, 47, 50, 58, 61, 101), and has been considered in Section II,B on Preparation.

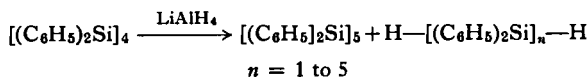
The cleavage of hexaaryldisilanes with organolithium reagents has been observed; however, this is not a particularly facile reaction (135, 136). In the cyclosilane series, octaphenylcyclotetrasilane (14, 137), decaphenylcyclopentasilane (14), and dodecamethylcyclohexasilane (14) are cleaved with organolithium reagents, whereas dodecaphenylcyclohexasilane (14, 101) is quite stable in the presence of these reagents.

Arylated disilanes have also been cleaved by silyllithium compounds (4, 5) and by lithium aluminum hydride in tetrahydrofuran (138). With the latter

reagent, a series of compounds, hexaphenyldisilane, 1,2-dimethyltetraphenyldisilane, tetramethyl-1,2-diphenyldisilane, and hexaethyldisilane, was treated in refluxing tetrahydrofuran for comparable lengths of time. The yields of the Si—H products decreased, respectively, as the number of phenyl substituents decreased, and no triethylsilane could be detected from hexaethyldisilane. These reactivities parallel the cleavage of the disilanes by lithium in tetrahydrofuran (4, 5). Evidence was obtained (138) which supports the following reaction sequence:

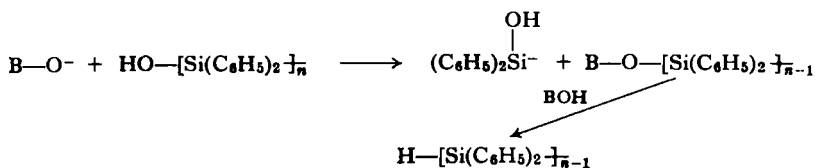


From the reaction of octaphenylcyclotetrasilane with lithium aluminum hydride, decaphenylcyclopentasilane, as well as a homologous series of  $\alpha,\omega$ -dihydropolysilanes, was isolated (138). Decaphenylcyclopentasilane is considerably less reactive toward lithium aluminum hydride (138).



The hydrogenolysis of some disilanes and octaphenylcyclotetrasilane has been reported (14, 138) to occur at relatively high temperatures and pressure in the presence of chromium-containing catalysts.

The cleavage of Si—Si bonds by alumina has been reported (14, 61a, 87). While the mechanism of this unusual and useful reaction has not been fully elucidated, the following scheme has been suggested (61a):

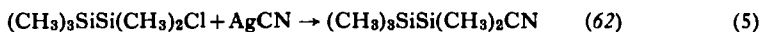
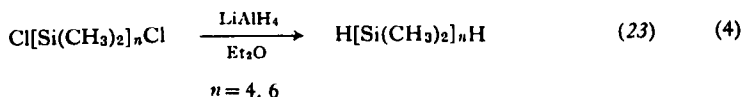
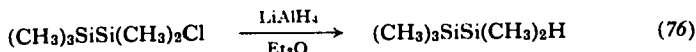
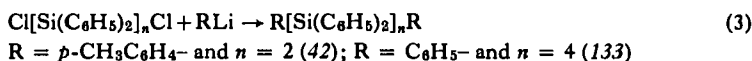
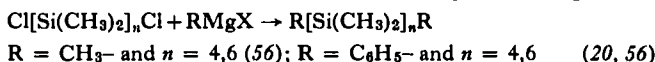
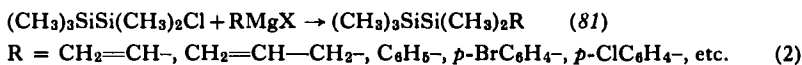
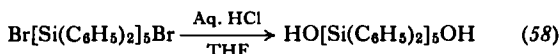
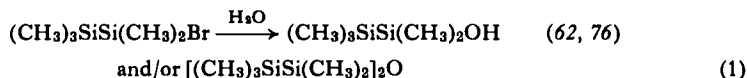


From published results it appears that when polysilanes (and possibly other catenated Group IVB compounds) have strongly electron withdrawing groups on the terminal silicon atoms they may be cleaved fairly specifically on a basic alumina column.

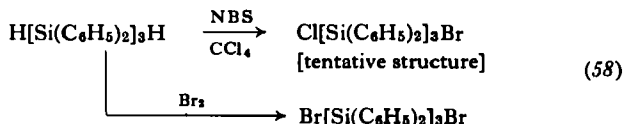
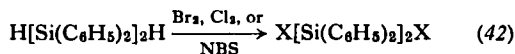
## 2. Reactions without Silicon-Silicon Bond Cleavage

The discovery of reactions which do not effect Si—Si bond cleavage is of prime importance to the continued growth of the chemistry of polysilanes.

In general, many reactions of functional monosilanes can also be used with polysilanes with little or no Si—Si cleavage. Thus, the Si—X bond in disilanes and higher polysilanes can be hydrolyzed (1) (2, 14), treated with Grignard reagents (2) (2, 14), organolithium reagents (3) (2, 14), lithium aluminum hydride (4) (2, 14, 56, 76), and inorganic salts (5) (2, 62) without cleavage of the Si—Si chain.

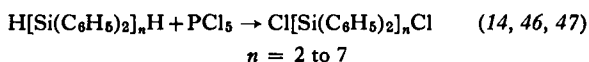


The Si—H group can be converted to the Si—X group by a variety of methods. In the disilane series, both halogens (42, 76) and *N*-bromosuccinimide (NBS) (42) have been used effectively. The same reagents have been employed with higher polysilanes (58).



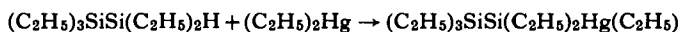
An extensive investigation of the conversion of silicon hydrides to chlorosilanes using phosphorus pentachloride (in  $\text{CCl}_4$ ) has been carried out (14,

139). This reagent appears to be an excellent choice for the halogenation of Si—H in polysilanes [phosphorus pentabromide has also been used (57)].



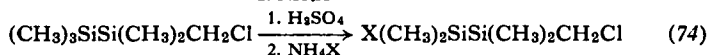
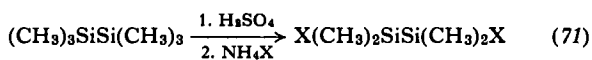
Recently, the peroxide or ultraviolet light-catalyzed addition of 1*H*-pentamethyldisilane and 1*H*,2*H*-tetramethyldisilane to olefins has been reported to proceed without Si—Si bond cleavage (69*a*). However, chloroplatinic acid-catalyzed reaction of 1*H*-pentamethyldisilane with olefins resulted in extensive cleavage of the Si—Si bond.

The preparation from the reaction of diethyl mercury and pentaethyldisilane of compounds containing the Si—Si—Hg linkage has been reported (83*b*).



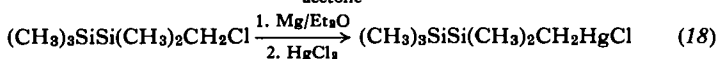
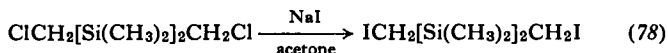
The reaction of hexaethyldisilane and benzoyl peroxide has been reported to give a product containing the Si—Si bond intact, and a dehydro dimer structure was assigned (41). Thus, the Si—Si bond is not cleaved, but rather polymerization occurs through detachment of hydrogen from organic groups. Similar reactions with higher polysilanes have not been reported.

The cleavage of Si—CH<sub>3</sub> bonds in hexaalkyldisilanes with concentrated sulfuric acid, followed by treatment with an ammonium halide has provided access to a variety of 1- and 1,2-halogenated disilanes (2). The course of the reaction can be followed by observation of the amount of methane evolved,



and this procedure has found numerous applications (2, 62, 64, 71, 74). This synthetic method is also applicable to higher polysilanes (18).

Carbon-functional disilanes react similarly to the corresponding monosilane derivatives. For example, the following reactions are typical for chloromethyl derivatives (2):



The preparation of chloromethyldisilanes has been accomplished with chlorine (ultraviolet light) (2), sulfuryl chloride (peroxides) (2), and *tert*-butyl hypochlorite (ultraviolet light) (77). The preparation and reactions of



carbon-functional higher polysilanes, however, have received little attention.

Disilanes containing the Si—O linkage have been treated with a variety of reagents such as Grignards (2), hydrogen fluoride (2), benzoyl chloride (2), and boron trifluoride (75) to give products with the Si—Si bond intact. Also, bis(pentamethyldisilanyl)amine reacts with boron trifluoride to give fluoropentamethyldisilane (75).

### III

## GERMANIUM

### A. Historical

In contrast to the other catenated Group IVB derivatives, the investigation of polygermanes did not have an early beginning which was followed by a period of quiescence. The first organic substituted digermane was not prepared until 1925 (142), and work has been relatively sparse even up to the present, although indications are that the pace is now quickening. An organotriggerman and tetragermane were prepared in 1930 (143), but only recently have other higher polygermanes been synthesized. Inorganic polygermanes were known before any organic derivatives, digermane and triggerman being prepared in 1924 (144).

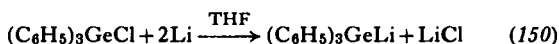
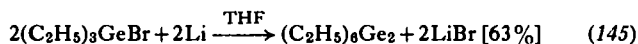
A problem which has continually plagued investigators in germanium chemistry has been the relatively high cost of all germanium derivatives. Efforts are being made, however, to promote study of germanium chemistry, and samples of germanium compounds are now much more readily available. The semiconductor properties of germanium have undoubtedly accounted for much interest in the element, and hopefully other uses will afford impetus for wider investigations of germanium chemistry.

### B. Preparation

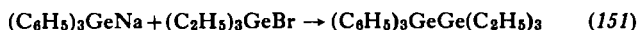
#### 1. From Halogermanes and Metals

Perhaps the most common method for the preparation of hexaorgano-digermanes is a Wurtz coupling of triorganogermanium halides with sodium (142, 145–148). The method may be employed with both alkyl- and arylgermanium halides. In the case of hexamethyldigermane, a satisfactory

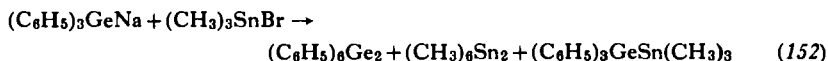
yield of product may be obtained by refluxing bromotrimethylgermane with potassium in the absence of solvent. Lithium may also be used with triethylgermanium halides in ether (149) or tetrahydrofuran (145, 149), but with chlorotriphenylgermane in tetrahydrofuran, the reaction leads to triphenylgermyllithium (150).



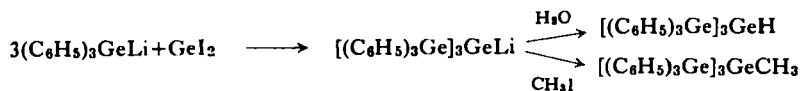
The triphenylgermylmetallic reagents are very versatile precursors of polygermanes. Of particular interest is the possibility of preparing unsymmetrically substituted digermanes (151, 151a). As might be anticipated,



the symmetrical hexaorganodigermane is frequently a side product in reactions of the metallic reagents, especially with halides which tend to undergo halogen-metal interconversion (150, 152-155).



Two reports have indicated the usefulness of the germylmetallics for the preparation of higher polygermanes. Octaphenyltrigermane has been obtained from the reaction of triphenylgermysodium with dichlorodiphenylgermane (156). Branched-chain polygermanes have been made available through the reaction of triphenylgermyllithium with germanium diiodide, which leads to tris(triphenylgermyl)germyllithium (156).



Germylmetallic compounds derived from transition metals are known (157), but have not yet found applications for the synthesis of polygermanes.

Diorganogermanium dihalides are among the most valuable precursors of polygermanes. Reaction of dibromodiphenylgermane with lithium amalgam leads to 1,2-dibromotetraphenyldigermane (158). The reaction of dichlorodiphenylgermane with sodium in xylene was first investigated in 1930 (143), and the product obtained has been subsequently identified (117) as



digermane (168). The reaction of ethyllithium with germanium tetrabromide produced low yields of both tetraethylgermane and hexaethyldigermane (163), while *n*-propyllithium with germanium tetrachloride gave only a *n*-propylgermanium polymer (169).

Another method of preparation starting from germanium tetrachloride has given mixed results. Reaction of the chloride with sodium and *p*-bromotoluene produces a reasonable yield of hexa-*p*-tolyl digermane along with some tetra-*p*-tolylgermane (146). Use of  $\beta$ -bromostyrene, however, gave hexa- $\beta$ -styryldigermane in only 0.5% yield (170).

A recent brief report (171) has indicated that reactions of organolithium or organomagnesium compounds with the dietherate of trichlorogermane,  $[(C_2H_5)_2O]_2 \cdot HGeCl_3$ , give rise to polygermanes. It is reported that both cyclogermanes and open-chain compounds are produced, but specific compounds are not named.

Germanium diiodide is also a useful precursor of polygermanes. As well as the one reaction mentioned earlier, the diiodide reacts with phenyllithium to produce a diphenylgermanium polymer (172). With di-*n*-butylmercury, the product is 1,2-diiodotetra-*n*-butyldigermane (173).

### 3. From Germanium Hydrides

A few reports have shown that germanium hydrides may be used to prepare polygermanes, but the real potential of the hydrides has not yet been made clear. Reaction of phenyllithium with triphenylgermane produces both tetraphenylgermane and hexaphenyldigermane, with the relative yields of the two products being dependent on reaction conditions (174). However, the interaction of triphenylgermyllithium with triphenylgermane leads to hexaphenyldigermane in only 12% yield (175).

Diphenylgermane,  $(C_6H_5)_2GeH_2$ , has been shown to react with diethylmercury to produce a germylmercury polymer which decomposes under the influence of heat or ultraviolet light to give octaphenylcyclotetragermane (159, 159a). It has also been demonstrated that bis[triethylgermyl]mercury is decomposed by ultraviolet light to produce hexaethyldigermane in 93.2% yield (176). These schemes employing germylmercury compounds may make possible the use of organic groups that would be reduced under the more vigorous conditions using alkali metals. A recent report has indicated that diethylzinc reacts with triethylgermane to produce polygermanes (176b).

Known organopolygermanes are summarized in Table II.

TABLE II  
ORGANOPOLYGERMANES

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Digermanes</i>			
C <sub>6</sub> H <sub>18</sub> Ge <sub>2</sub>	Hexamethyldigermane	− 40° (137°/772 mm) $n_D^{25}$ 1.4564	38, 79, 104
C <sub>10</sub> H <sub>25</sub> BrGe <sub>2</sub>	Bromopentaethyldigermane	—	176a
C <sub>10</sub> H <sub>25</sub> ClGe <sub>2</sub>	Chloropentaethyldigermane	(120°–127°/17 mm) $n_D^{20}$ 1.5015	176b
C <sub>12</sub> H <sub>10</sub> Br <sub>4</sub> Ge <sub>2</sub>	Tetrabromo-1,2-diphenyldigermane	115°–119°	158
C <sub>12</sub> H <sub>18</sub> Ge <sub>2</sub>	Hexavinyldigermane	(55°/0.35–0.25 mm) $n_D^{25}$ 1.5217	164, 177
C <sub>12</sub> H <sub>30</sub> Ge <sub>2</sub>	Hexaethyldigermane	(266.3°/760 mm) $n_D^{20}$ 1.4960	145, 149, 163, 176, 178
C <sub>16</sub> H <sub>36</sub> Ge <sub>2</sub> I <sub>2</sub>	Tetra- <i>n</i> -butyl-1,2-diiododigermane	—	173
C <sub>17</sub> H <sub>30</sub> Ge <sub>2</sub> O <sub>2</sub>	Benzoylpentaethyldigermane	(140°–146°/2 mm) $n_D^{20}$ 1.5287	176b
C <sub>20</sub> H <sub>26</sub> Ge <sub>2</sub>	Bis(cyclotetramethylene)diphenyldigermane	(176°/0.6 mm) $n_D^{20}$ 1.6085	148
C <sub>24</sub> H <sub>20</sub> Br <sub>2</sub> Ge <sub>2</sub>	1,2-Dibromotetraphenyldigermane	167°–169°	158
C <sub>24</sub> H <sub>30</sub> Ge <sub>2</sub>	1,1,1-Triethyltriphenyldigermane	89.5°–90.5°	151
C <sub>26</sub> H <sub>26</sub> Ge <sub>2</sub>	1,2-Dimethyltetraphenyldigermane	—	159a
C <sub>27</sub> H <sub>36</sub> Ge <sub>2</sub>	1,1,1-Tribenzyltriethyldigermane	63.5°–64.5°	151a
C <sub>28</sub> H <sub>30</sub> Ge <sub>2</sub>	1,2-Diethyltetraphenyldigermane	125°–126.5°	151a

$C_{36}H_{30}Ge_2$	Hexaphenyldigermane	352°–354°	92, 93, 142, 146, 150, 152, 156, 166, 167, 179
$C_{36}H_{66}Ge_2$	Hexacyclohexyldigermane	316° (dec)	147
$C_{42}H_{42}Ge_2$	Hexabenzyl digermane	183°–184°	146
$C_{42}H_{42}Ge_2$	Hexa- <i>o</i> -tolyl digermane	284°–286°	167
$C_{42}H_{42}Ge_2$	Hexa- <i>m</i> -tolyl digermane	177°–179°	167
$C_{42}H_{42}Ge_2$	Hexa- <i>p</i> -tolyl digermane	345°	146, 167
$C_{48}H_{42}Ge_2$	Hexa- $\beta$ -styryl digermane	230°–232°	170
<i>Polygermanes</i>			
$C_{41}H_{42}Ge_3$	Butylmethylbis(triphenylgermyl)germane	187°–190°	156
$C_{48}H_{40}Ge_3$	Octaphenyltrigermane	247°–248°	143
$C_{48}H_{40}Ge_4$	Octaphenylcyclotetragermane	238° (dec). 294°–295°	117, 143, 159, 159a
$C_{48}H_{40}Ge_4I_2$	1,4-Diiodoctaphenyltetragermane	—	117, 159a
$C_{48}H_{40}Ge_4O$	Octaphenyloxacyclopentagermane	206°–207°	117, 159a
$C_{50}H_{46}Ge_4$	1,4-Dimethyloctaphenyltetragermane	189°–191°	159a
$C_{54}H_{46}Ge_4$	Tris(triphenylgermyl)germane	192°–194°	156
$C_{55}H_{48}Ge_4$	Methyltris(triphenylgermyl)germane	194°–196°	156
$C_{60}H_{50}Ge_4$	Decaphenyltetragermane	274°–276°	117, 159, 159a
$C_{60}H_{50}Ge_5$	Decaphenylcyclopentagermane	> 360°	117, 159, 159a
$C_{12}H_{36}Ge_6$	Dodecamethylcyclohexagermane	211°–213°	160
$C_{72}H_{60}Ge_6$	Dodecaphenylcyclohexagermane	> 360°	117, 159, 159a

<sup>a</sup> Boiling point values are given in parentheses.

### C. Physical Properties

#### 1. General

The lower alkyl digermanes are normally liquids, while phenylated digermanes are solids. In the one known instance of a completely alkylated higher polygermane, dodecamethylcyclohexagermane is a high-melting solid, m.p. 211°–213° C (160). Most polygermanes are quite stable to heat. For instance, hexaphenyldigermane melts at 352°–354° C without decomposition (167), and hexaethyldigermane may be distilled in air at 265° C (178). There are isolated instances of decomposition at lower temperatures. Octaphenylcyclotetragermane decomposes on melting at 238° C (159), while the analogous five- and six-membered rings do not melt or decompose below 360° C (117). Hexacyclohexyldigermane decomposes on melting at 316° C (147).

#### 2. Spectral

A number of spectral studies have been published in recent years. The Raman spectrum of hexamethyldigermane has been analyzed (104), and digermane itself has been studied by both Raman and infrared spectroscopy (180). Other interesting infrared studies include the observation of shifts in the Ge—H stretching and bending modes in the series of homologs from  $\text{Ge}_2\text{H}_6$  to  $\text{Ge}_5\text{H}_{12}$  (181–183), and the 15–35  $\mu$  spectrum of hexaphenyldigermane (93). Glockling and co-workers have tentatively attributed bands in the 228–234  $\text{cm}^{-1}$  region to the Ge—Ge stretching vibration (151a, 156). Recently, the ultraviolet spectra of the known perphenylated cyclogermanes were published (117), and that of hexaphenyldigermane (92) was taken to indicate intense interaction of phenyl groups on different Ge atoms through *d* orbital overlap through the Ge—Ge bond.

Several nuclear magnetic resonance studies have also been made. The spectra of the hydrides, trigermane and *n*- and isotetragermane, have been published (181). The  $\text{GeH}_2$  protons in trigermane are shifted upfield 0.193 ppm relative to the  $\text{GeH}_3$  protons. The corresponding shift in trisilane is 0.167 ppm, while the shift for propane is 0.438 ppm downfield. The explanation offered for the differences is that the order of electronegativities is  $\text{C} > \text{H} > \text{Si} \approx \text{Ge}$ . The GeH proton in isotetragermane could not be seen in the spectrum of that compound, but the coupling constant,  $J_{\text{GeH}, \text{GeH}_2}$ , was found to be 4 cps [ $J_{\text{CH}, \text{CH}_2} = 5$  cps] (181). The spectrum of hexavinyl-digermane has been analyzed (177), and the vinyl hydrogen coupling

constants were found to be smaller than those for vinylsilanes, indicating a greater electronegativity for germanium than for silicon (177). The spectrum of hexamethyldigermane was compared with that of tetramethylgermane, showing decreased shielding in the former (79).

### 3. Bond Energy

Two methods have been used to determine the germanium-germanium bond energy. The heat of combustion of hexaethyldigermane was measured and a bond energy of 62 kcal mole<sup>-1</sup> calculated (184). A rather different result was obtained through measurement of the heat of explosive decomposition of digermane in the presence of stibine. In that case, the Ge—Ge bond energy was calculated to be 37.9 kcal mole<sup>-1</sup> (122). However, there has been no indication in the literature of a tendency toward homolytic dissociation of the germanium-germanium bond into germyl radicals. The magnetic susceptibility of hexaphenyldigermane in powder form and in benzene solution has been measured, and a small upper limit of dissociation was observed (179). The opinion is expressed (179) that it is improbable that any dissociation takes place under these conditions.

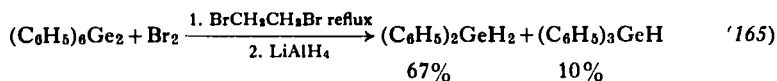
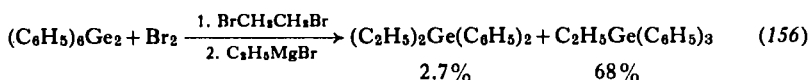
## D. Chemical Properties

### 1. Reactions with Electrophilic and Oxidative Reagents

Oxidative cleavage of the germanium-germanium bond, with the exception of cleavage by halogens, has been rather sparingly investigated, and the reactions which have been tried are not very facile. Virtually all organic polygermanes are stable in air, and hexaphenyldigermane in benzene does not react with oxygen (185). Reaction with alcoholic silver nitrate, which is a common qualitative test for the tin-tin bond, occurs only slowly with hexaphenyldigermane in boiling solution (142). The reaction has not been attempted with alkylpolygermanes, which presumably would be more reactive.

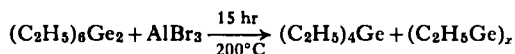
Bromine cleaves polygermanes rather readily to form bromogermanes (143, 152, 156, 164, 165, 178). Both alkyl- and aryl-substituted polygermanes undergo the reaction. When hexaphenyldigermane is reacted with bromine in refluxing carbon tetrachloride, only bromotriphenylgermane is isolated (152), while the same reaction in 1,2-dibromoethane apparently leads to dibromodiphenylgermane as well as the primary cleavage product.





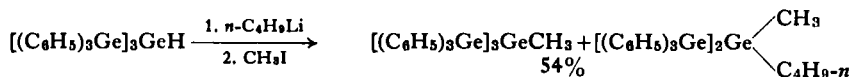
Cleavage by iodine proceeds normally with hexavinyl digermane to produce iodotrivinylgermane (164), but hexaphenyldigermane is not affected by iodine in refluxing chloroform (185). Even in refluxing xylene 40% of hexaphenyldigermane was recovered, while the only other product obtained was hexaphenyldigermoxane (185). The two cyclogermanes, decaphenylcyclopentagermane and dodecaphenylcyclohexagermane, are also inert towards iodine in benzene, although the more reactive octaphenylcyclotetragermane is cleaved to afford 1,4-diiodooctaphenyltetragermane (117, 159a).

In common with the hexaalkyl derivatives of tin and lead, hexaethyl digermane disproportionates in the presence of Lewis acid catalysts (176a).

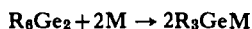


## 2. Reactions with Nucleophilic and Reductive Reagents

Cleavage of the germanium-germanium bond by nucleophilic reagents occurs with some facility. Hexa- $\beta$ -styryldigermane reacts slowly with aqueous sodium hydroxide (170), whereas hexaphenyldigermane is inert to boiling aqueous alkali (142). At least in the latter case the lack of solubility of the digermane must be an important factor. 1,4-Diiodooctaphenyltetragermane is converted to a compound which is apparently octaphenyloxacyclopentagermane, the transformation evidently occurring without appreciable Ge—Ge bond cleavage (117, 159a). Likewise, the 1,4-diiodo derivative reacts with phenyllithium to afford decaphenyltetragermane (159, 159a). Some cleavage does occur, however, in the reaction of tris (tri-phenylgermyl)-germane with *n*-butyllithium (156).



The germanium-germanium bond is rather generally susceptible to cleavage by alkali metals, to form germymetallic species.



The earliest investigators of this reaction used sodium in liquid ammonia to convert hexaphenyldigermane to triphenylgermysodium (152). In like manner, hexaethyldigermane affords metallic derivatives with sodium in liquid ammonia-ether mixture or potassium in ethylamine (178). Trigermane,  $\text{Ge}_3\text{H}_8$ , is apparently cleaved by sodium in ammonia to give the two expected sodium derivatives,  $\text{H}_3\text{GeNa}$  and  $\text{H}_2\text{GeNa}_2$ , as primary products, but other reactions occur following this initial cleavage (183). Attempts to cleave hexaalkyldigermanes with alkali metals using ethers as solvents (38, 149), or refluxing hexaethyldigermane with sodium in the presence of bromotriethylsilane (145), gave only unreacted digermane. In contrast, hexaphenyldigermane affords metallic derivatives with sodium-potassium alloy in ether-tetrahydrofuran (185, 186) [not, however, in ether alone (185)], lithium in ethylene glycol dimethyl ether (185) or tetrahydrofuran (150), and potassium in ethylene glycol dimethyl ether or xylene (185). Hexabenzoyldigermane affords tribenzylgermyllithium on cleavage with the metal in ethylene glycol dimethyl ether (151a). The cyclogermane, octaphenylcyclotetragermane, is cleaved by lithium (117, 159a). Treatment of the reaction mixture with bromobenzene afforded decaphenyltetragermane along with some decaphenylcyclopentagermane. Conversion of the cyclotetragermane to cyclopentagermane by the action of lithium is perhaps to be expected since the same transformation occurs with the perphenylated cyclosilanes (14). Diphenylgermyldisodium is reported to be formed on cleavage of octaphenylcyclotetragermane with sodium in liquid ammonia (143), however, the reagent has not been exploited for synthetic purposes.

## IV

## TIN

### A. Historical

The chemistry of catenated organotin compounds began as early as 1852 with the report by Löwig (187) of the reaction of ethyl iodide with tin-sodium alloy. A product of this reaction, a diethyltin polymer, has only very recently been characterized (11, 159, 188). A similar situation may be cited in the case of tetrakis (triphenylstannyl) tin which was prepared as early as 1923 (189), but was not rigorously identified until 1964 (15, 190). This compound is the only discrete branched-chain polytin in the literature at present. These two examples are not entirely representative of the state of the science in

catenated tin chemistry, but they are indicative of the current active interest in the field and of the kind of fundamental questions which are only now being given answers.

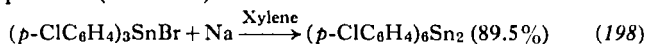
As may be noted in Table III, the ditin compounds known outnumber the higher polytins. This is in part due undoubtedly to the greater difficulty of synthesizing some of the latter compounds. The pioneer in this area, C. A. Kraus, characterized the first tritin and pentatin derivatives in 1925 (191), but his work was not elaborated upon until recent years. The synthetic possibilities have now been broadened considerably by the characterization of cyclic polytin compounds, which may serve as precursors for many new derivatives. Any number of fundamental questions bearing upon the effects of chain length in catenated tin compounds may find answers in the near future.

A particularly active area of investigation is that concerned with the nature of "divalent" tin species,  $R_2Sn$ . It has now been well established that these compounds are in many cases polymers of the  $R_2Sn$  structure, and are not, in fact, tin species in the divalent state. Some diorganotin compounds, particularly those prepared from organolithium or organomagnesium reagents and stannous chloride, have been shown (11, 188, 192-194) to correspond to  $R_2Sn$  compounds only in gross composition, and to contain tin polymers with chain-branching, so that  $R_3Sn-$  and  $RSn\leq$  moieties are present in the compounds. Reviews (11, 194a) of the nature of these compounds and the problems involved in their study have recently appeared, so that the present writing will in the main treat only those compounds which have been shown to be reasonably discrete species.

## B. Preparation

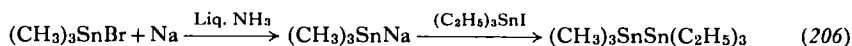
### 1. From Tin Halides

Almost every useful method for the synthesis of organopolytin compounds has involved organotin halides or hydrides as starting materials. The classic Wurtz synthesis employing a triorganotin halide and sodium in benzene, toluene, or xylene has been used frequently for the preparation of ditin compounds (195-200).

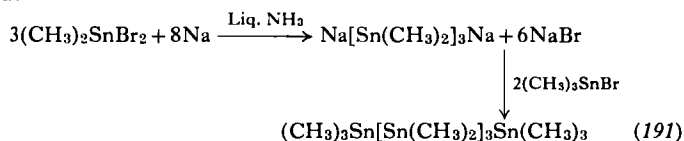


Other solvents, such as diethyl ether (201), isoamyl ether (202, 203), or ethanol (195, 204) have been successfully employed, or the reaction may be

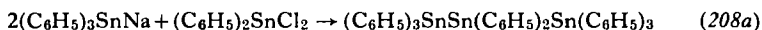
run using sodium powder and a liquid organotin halide without solvent (201). Another solvent which has been shown to have considerable versatility is liquid ammonia. A simple coupling may be accomplished with a triorganotin halide and lithium (205) or sodium (205–208) in liquid ammonia. But, more importantly, the reaction may be halted with the formation of a triorganotin sodium compound, which may be treated subsequently with a different triorganotin halide to obtain an unsymmetrical ditin (206, 207).



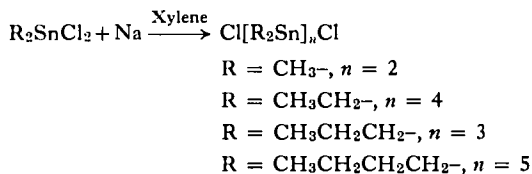
The versatility does not end here, however, for diorganotin dihalides may be reacted with sodium to produce polytin sodium compounds (191, 209, 210). Thus, Kraus has shown that proper choice of the ratio of sodium to dimethyltin dibromide leads to 1,2-disodiotetramethylditin or 1,3-disodiohexamethyltritin. Using this method a chain of five tin atoms has been obtained.



Triphenyltin sodium in ethylene glycol dimethyl ether has also been used to prepare a tritin.

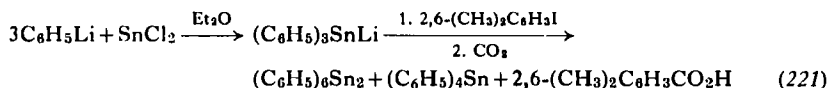


In one case a discrete polymer, dodecamethylcyclohexatin, has been obtained (211) from the reaction of dimethyltin dichloride with sodium in liquid ammonia. Using diorganotin dichlorides and sodium in xylene,  $\alpha,\omega$ -dichloropolytin compounds may be obtained in yields of up to 50% (212). One major product was obtained from each tin halide; dimethyltin dichloride produced a ditin; diethyl-, dipropyl-, and dibutyltin dichloride gave tetratin, tritin, and pentatin, respectively (212).



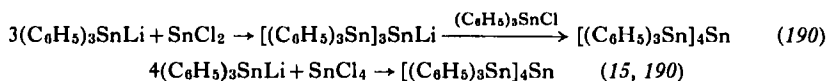
A number of additional preparations involving alkali metals have been reported. The first preparation of a hexaorganoditin involved the addition

of ethyl iodide to a tin-sodium alloy to produce what appears to be hexaethyl-ditin, along with other products (187, 213). Tin-sodium alloy has also been reacted with organomercuric halides to produce a hexa-substituted ditin along with tetra-substituted tin (214). A phenoxy group attached to tin serves as a pseudohalogen in the reaction of trimethylphenoxytin with sodium in liquid ammonia, the product being hexamethylditin (209). Trimethyltin hydroxide also may be used in the coupling reaction to produce hexamethylditin (208, 215). Reaction of triphenyltin chloride with potassium graphite ( $\text{KC}_8$ ) leads to hexaphenylditin (216). Triorganotinlithium reagents, obtained on treatment of stannous chloride (199, 217) or  $\text{R}_2\text{Sn}$  compounds (205) with an organolithium compound in ether or by direct reaction of  $\text{R}_3\text{SnCl}$  with lithium in tetrahydrofuran (218–220), disproportionate under a variety of conditions to produce the corresponding hexa-organoditin. Hydrolysis (199, 218–220) or carbonation (199, 219) of a tinlithium reagent leads to the ditin, as does reaction of a triorganotinlithium or -sodium compound with organic halides which can undergo halogen-metal interconversion (218, 221–223).



The lithium reagents may be used to make unsymmetrical ditin compounds (220) just as the sodium reagents, thus avoiding the use of liquid ammonia.

The reaction of an organolithium compound with stannous chloride often leads to polymeric diorganotin species of indefinite composition (11). In two cases relatively discrete compounds, eicosaethylcyclodecatin and hexadeca-*n*-butylcyclooctatin, appear to have been obtained (224). Treatment of stannous chloride with a Grignard reagent may lead directly to the hexaorganoditin (195, 200). A rather thorough investigation of the products of the interaction of stannous chloride with phenylmagnesium bromide in a 1:6 molar ratio showed the presence of three products: hexaphenylditin, tetraphenyltin, and tetrakis (triphenylstannyl) tin (15, 189, 190). The latter compound has subsequently been synthesized by independent means.



In a synthesis which is unique, octa-*tert*-butylcyclotetratin has been obtained from di-*tert*-butyltin dichloride and *tert*-butylmagnesium chloride

(225). The reaction does not lead to the normal product, tetra-*tert*-butyltin, probably for steric reasons.

Hexaphenylditin has also been obtained by electrolysis of a methanol solution of triphenyltin chloride, the product being produced at the cathode (226). Other triorganotin halides have been electrolyzed in aqueous isopropanol, but the ditin compounds thought to be produced were not isolated (227).

In two cases, attempted reduction of triaryltin chlorides with lithium aluminum hydride led to ditins instead of the expected tin hydrides (227a).

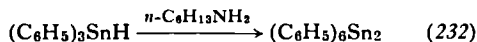
## 2. From Tin Hydrides

A variety of synthetic methods employs tin hydrides as the starting materials. The interaction of triethyltin hydride with diethylmercury leads to hexaethylditin, mercury, and ethane (228). Hexamethylditin has been obtained by treatment of dimethyltin dihydride with sodium in liquid ammonia, followed by addition of methyl iodide.



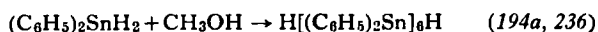
Simple pyrolysis of the same dihydride produces some hexamethylditin, but the reaction is complex and appears to be of little synthetic utility (230).

Reactions of triorganotin hydrides with amines lead to the corresponding ditin (231–235).

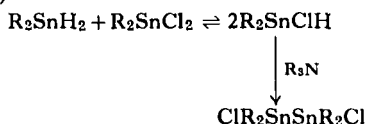


It was originally thought that the reaction was a deamination, but more recent work indicates that the action of the amine is catalytic, no hydrocarbon or ammonia being formed (234, 235). As expected, preformed stannylamines condense with tin hydrides to form tin—tin bonds (235a–235e). Quite recently this reaction has been investigated mechanistically, and a polar reaction involving electrophilic attack of the hydride on nitrogen is indicated (235e).

In an interesting extension of the above reactions, diorganotin dihydrides have been treated with amines to obtain cyclic polytin compounds (159, 188, 192, 194a, 236, 236b, 236c). In one reported case (188) a 94% yield of octadecaethylcyclononatin was obtained from diethyltin dihydride and a pyridine–diethyltin dichloride complex. It is apparently also possible to obtain straight-chain products with suitable reagents.



Still another variation in the above reactions has afforded 1,2-dichlorotetraalkylditins (236a).

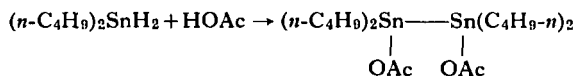


Further adaptations (235b–235d) have led to specific syntheses of higher polytin compounds, both symmetrically and unsymmetrically substituted.

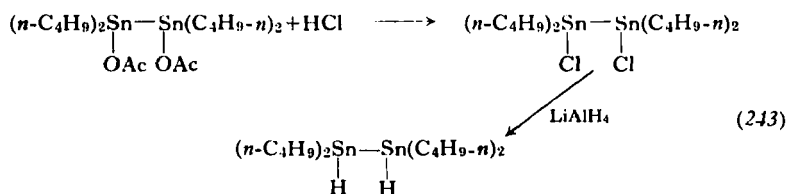
Tin hydrides also react with tin oxides to afford di- and polytin compounds (237a, 237b). The method may be adapted to produce either symmetrical or unsymmetrical ditins. Indeed, a variety of electronegative substituents attached to tin may be displaced by tin hydrides to form tin–tin bonds (237a).

Reductions of ketones, sulfones, and sulfoxides with triphenyltin hydride have been shown to give hexaphenylditin as the tin-containing product (232, 237). Isocyanates or isothiocyanates (238, 239) as well as benzoyl peroxide (239a) also produce the same product from triphenyltin hydride. In contrast, however, alkyltin hydrides undergo addition to carbonyl groups to form alkyltin alkoxides (239b).

A potentially quite useful synthetic method was recently reported by Sawyer and Kuivila (240–242), who treated diorganotin dihydrides with carboxylic acids to obtain functionally substituted ditin compounds. Thus, the reaction of dibutyltin dihydride with acetic acid leads to 1,2-diacetoxytetra-*n*-butylditin in 65% yield.



The acetoxy groups may be replaced by halogen through treatment with hydrogen chloride in ether, and the dihalide reduced with lithium aluminum hydride, all without scission of the tin–tin bond.



The same diacetoxyditin was prepared from the interaction of dibutyltin dihydride and dibutyltin diacetate (240, 241). In the same papers another

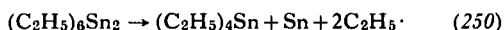
method was found to be successful, namely, treatment of diphenyltin with benzoyl peroxide to produce 1,2-dibenzoyloxytetraphenylditin in 81% yield (240, 241).

The cyclic polytin compounds have not as yet been used extensively for synthetic purposes, but indicative of what might be done is the reaction of octa-*tert*-butylcyclotetratin with iodine to prepare 1,4-diiodoocta-*tert*-butyltetratin (225). Some limitations to the synthetic possibilities of the cyclostannanes have been noted by Neumann (194a).

### C. Physical Properties

The lower molecular weight hexaalkylditins are generally rather high boiling liquids, while the compounds containing aryl groups are solids. The hexaorganoditins are generally soluble in aromatic solvents, less so in chloroform or ether, and insoluble in ethanol.

The known polytins appears to be reasonably stable to heat. In an isolated example, hexamethylditin has been observed to decompose in boiling benzene (204). It is likely that this observation is due to the presence of an impurity or to air oxidation, since the compound has been reported to distil at 182° C apparently without decomposition (206). Normally temperatures above 250° C are required, and several aryl and alkyl derivatives have been observed to deposit tin under these conditions (195, 224, 248–250). A method for decomposing hexaethyl- and hexaphenylditin at 1000° F in order to obtain a tin coating has been patented (248). The thermal decomposition of hexaethylditin at 275° C may be represented as follows:



It is likely that the first stage in the process is the conversion of the ditin to tetraethyltin and diethyltin, the latter producing tin and two ethyl radicals (250).

For a number of years, the ditins were thought to be considerably dissociated in solution into triorganotin radicals. Molecular weight determinations on several ditins corresponded to almost complete dissociation at low concentrations in benzene or ether solution (189, 206, 251). However, cryoscopic molecular weight determinations on hexamethylditin in benzene (207) and hexaphenylditin in camphor (189) indicated the dimeric structure. Magnetic susceptibility measurements on hexamethylditin and even hexa-*o*-tolyllditin indicated no dissociation (204, 252). It seems quite unlikely that



TABLE III  
ORGANOPOLYTINS

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Ditins</i>			
C <sub>4</sub> H <sub>12</sub> Cl <sub>2</sub> Sn <sub>2</sub>	1,2-Dichlorotetramethylditin	186° (dec)	212
C <sub>6</sub> H <sub>18</sub> Sn <sub>2</sub>	Hexamethylditin	23° (182°/756 mm)	191, 206, 207, 209, 215, 229
C <sub>9</sub> H <sub>24</sub> Sn <sub>2</sub>	1,1,1-Triethyltrimethylditin	(235°/748 mm)	206
C <sub>12</sub> H <sub>30</sub> Sn <sub>2</sub>	Hexaethylditin	(160°/23 mm)	201–203, 208
		$n_D^{17.8}$ 1.53738	210, 228, 244,
C <sub>14</sub> H <sub>34</sub> Sn <sub>2</sub>	Tetraethyl-1,2-di- <i>n</i> -propylditin	(165.8°/15 mm)	201
		$n_D^{15.3}$ 1.53541	
C <sub>16</sub> H <sub>36</sub> Cl <sub>2</sub> Sn <sub>2</sub>	Tetra- <i>n</i> -butyl-1,2-dichloroditin	—	243
C <sub>16</sub> H <sub>38</sub> Sn <sub>2</sub>	1 <i>H</i> ,2 <i>H</i> -Tetra- <i>n</i> -butylditin	$n_D^{25}$ 1.5205	243
C <sub>16</sub> H <sub>38</sub> Sn <sub>2</sub>	Tetraethyl-1,2-diisobutylditin	(179°/15.5 mm)	201
		$n_D^{19.8}$ 1.52571	
C <sub>18</sub> H <sub>42</sub> Sn <sub>2</sub>	Hexa- <i>n</i> -propylditin	(143.6°/15 mm)	201
		$n_D^{19.5}$ 1.52583	
C <sub>18</sub> H <sub>42</sub> Sn <sub>2</sub>	1,1,1-Tri- <i>n</i> -butyltriethylditin	(109°/0.2 mm)	235c
C <sub>18</sub> H <sub>42</sub> Sn <sub>2</sub>	1,1,1-Triisobutyltriethylditin	(117°/0.3 mm)	235c, 237a
C <sub>20</sub> H <sub>42</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Diacetoxytetra- <i>n</i> -butylditin	–7° to –4°	240, 241, 243
		$n_D^{26}$ 1.5060	
C <sub>21</sub> H <sub>24</sub> Sn <sub>2</sub>	1,1,1-Trimethyltriphenylditin	107°–108.5°	207, 220
C <sub>22</sub> H <sub>52</sub> N <sub>2</sub> Sn <sub>2</sub>	1,2-Bis(γ-aminopropyl)tetraisobutylditin	—	236a
C <sub>24</sub> H <sub>30</sub> Sn <sub>2</sub>	1,1,1-Trimethyltri- <i>p</i> -tolyliditin	139.5°–141°	38
C <sub>24</sub> H <sub>30</sub> Sn <sub>2</sub>	1,1,1-Triethyltriphenylditin	16°	235b, 237a
		$n_D^{20}$ 1.6327	

C <sub>24</sub> H <sub>54</sub> Sn <sub>2</sub>	Hexa- <i>n</i> -butylditin	(156°–160°/0.025 mm) $n_D^{25}$ 1.5090	220, 245, 246
C <sub>24</sub> H <sub>54</sub> Sn <sub>2</sub>	Hexaisobutylditin	56° (130°/0.15 mm)	201, 235c
C <sub>28</sub> H <sub>20</sub> Cl <sub>6</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis(trichloroacetoxy)tetraphenylditin	170°	240, 241
C <sub>28</sub> H <sub>20</sub> F <sub>6</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis(trifluoroacetoxy)tetraphenylditin	165°	240, 241
C <sub>28</sub> H <sub>22</sub> Cl <sub>4</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis(dichloroacetoxy)tetraphenylditin	169°	240, 241
C <sub>28</sub> H <sub>24</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis(chloroacetoxy)tetraphenylditin	150°	240, 241
C <sub>28</sub> H <sub>26</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Diacetoxytetraphenylditin	152°	240, 241
C <sub>30</sub> H <sub>42</sub> Sn <sub>2</sub>	1,1,1-Tri- <i>n</i> -butyltriphenylditin	$n_D^{20}$ 1.5978	235b
C <sub>30</sub> H <sub>42</sub> Sn <sub>2</sub>	1,1,1-Triisobutyltriphenylditin	79°	235c
C <sub>30</sub> H <sub>44</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis( <i>o</i> -chlorobenzoyloxy)tetra- <i>n</i> -butylditin	65°–66.5°	240, 241
C <sub>30</sub> H <sub>44</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis( <i>p</i> -chlorobenzoyloxy)tetra- <i>n</i> -butylditin	75°–77°	240, 241
C <sub>30</sub> H <sub>46</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Dibenzoyloxytetra- <i>n</i> -butylditin	31.5°–32.5°	240, 241
C <sub>30</sub> H <sub>66</sub> Sn <sub>2</sub>	Hexaneopentylditin	275°–277°	246a
C <sub>36</sub> H <sub>24</sub> Cl <sub>6</sub> Sn <sub>2</sub>	Hexa- <i>p</i> -chlorophenylditin	224°–226°	198, 214
C <sub>36</sub> H <sub>30</sub> Sn <sub>2</sub>	Hexaphenylditin	237°	195, 205, 217, 219, 223, 226, 231, 237
C <sub>36</sub> H <sub>42</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Dihexanoyloxytetraphenylditin	85°–87°	240, 241
C <sub>36</sub> H <sub>66</sub> Sn <sub>2</sub>	Hexacyclohexylditin	—	196
C <sub>38</sub> H <sub>28</sub> Cl <sub>2</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Bis( <i>o</i> -chlorobenzoyloxy)tetraphenylditin	161°	240, 241
C <sub>38</sub> H <sub>30</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Dibenzoyloxytetraphenylditin	184°–185°	240, 241
C <sub>38</sub> H <sub>30</sub> O <sub>6</sub> Sn <sub>2</sub>	1,2-Bis( <i>o</i> -hydroxybenzoyloxy)tetraphenylditin	197°	240, 241
C <sub>40</sub> H <sub>50</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Dioctanoyloxytetraphenylditin	86°–88°	240, 241
C <sub>40</sub> H <sub>82</sub> O <sub>4</sub> Sn <sub>2</sub>	1,2-Dilauroyloxytetra- <i>n</i> -butylditin	—	241
C <sub>42</sub> H <sub>24</sub> F <sub>18</sub> Sn <sub>2</sub>	Hexakis( <i>m</i> -trifluoromethylphenyl)ditin	100.6°–101.9°	227a
C <sub>42</sub> H <sub>42</sub> Sn <sub>2</sub>	Hexa- <i>p</i> -tolyliditin	145°, 251°–252°	38, 195
C <sub>42</sub> H <sub>42</sub> Sn <sub>2</sub>	Hexa- <i>o</i> -tolyliditin	298°–300°, 208°–210°	199, 204
C <sub>42</sub> H <sub>42</sub> Sn <sub>2</sub>	Hexabenzyliditin	147°–148°	197
C <sub>42</sub> H <sub>66</sub> Sn <sub>2</sub>	1,1,1-Tri- <i>n</i> -octyltriphenylditin	$n_D^{20}$ 1.5599	235b
C <sub>48</sub> H <sub>54</sub> Sn <sub>2</sub>	Hexa- <i>p</i> -xylylditin	196°	195
C <sub>72</sub> H <sub>54</sub> Sn <sub>2</sub>	Hexa-2-biphenylylditin	170°, 288°–289°	200

TABLE III—continued

Formula	Name	M.p. (b.p.) <sup>a</sup> (° C)	Reference
<i>Polytins</i>			
C <sub>8</sub> H <sub>24</sub> Sn <sub>3</sub>	Octamethyltritin	—	211
C <sub>10</sub> H <sub>28</sub> Sn <sub>3</sub>	1,3-Diethylhexamethyltritin	—	191
C <sub>14</sub> H <sub>36</sub> Sn <sub>3</sub>	Hexaethyl-2,2-dimethyltritin	(114°/0.001 mm)	235c
C <sub>16</sub> H <sub>40</sub> Sn <sub>3</sub>	Octaethyltritin	(118°/0.001 mm) $n_D^{20}$ 1.5894	235c, 235d, 237a
C <sub>18</sub> H <sub>42</sub> Cl <sub>2</sub> Sn <sub>3</sub>	1,3-Dichlorohexa- <i>n</i> -propyltritin	122°	212
C <sub>18</sub> H <sub>28</sub> Sn <sub>3</sub>	2,2-Diphenylhexamethyltritin	$n_D^{20}$ 1.6624	235b
C <sub>20</sub> H <sub>48</sub> Sn <sub>3</sub>	2,2-Di- <i>n</i> -butylhexaethyltritin	(133°/0.001 mm) $n_D^{20}$ 1.5641	235c, 237a
C <sub>20</sub> H <sub>48</sub> Sn <sub>3</sub>	2,2-Diisobutylhexaethyltritin	(136°/0.001 mm)	235c
C <sub>24</sub> H <sub>40</sub> Sn <sub>3</sub>	2,2-Diphenylhexaethyltritin	$n_D^{20}$ 1.6202	235b
C <sub>30</sub> H <sub>60</sub> Sn <sub>3</sub>	2 <i>H</i> , 2-Phenylhexa- <i>n</i> -butyltritin	$n_D^{20}$ 1.5712	235d
C <sub>32</sub> H <sub>72</sub> Sn <sub>3</sub>	Octa- <i>n</i> -butyltritin	(165°/0.001 mm)	235c
C <sub>32</sub> H <sub>72</sub> Sn <sub>3</sub>	Octaisobutyltritin	— 7°, (170°/0.001 mm)	235c
C <sub>36</sub> H <sub>64</sub> Sn <sub>3</sub>	2,2-Diphenylhexa- <i>n</i> -butyltritin	$n_D^{20}$ 1.5886	235b
C <sub>38</sub> H <sub>60</sub> Sn <sub>3</sub>	Penta- <i>n</i> -butyl-1,1,1-triphenyltritin	$n_D^{20}$ 1.6002	235d
C <sub>40</sub> H <sub>40</sub> Sn <sub>3</sub>	Pentaethyl-1,1,1-triphenyltritin	$n_D^{20}$ 1.6516	235b
C <sub>44</sub> H <sub>48</sub> Sn <sub>3</sub>	2,2-Di- <i>n</i> -butylhexaphenyltritin	$n_D^{20}$ 1.6452	235b
C <sub>48</sub> H <sub>40</sub> Sn <sub>3</sub>	Octaphenyltritin	280° (dec)	208a
C <sub>60</sub> H <sub>112</sub> Sn <sub>3</sub>	2,2-Diphenylhexa- <i>n</i> -octyltritin	$n_D^{20}$ 1.5420	235b
C <sub>10</sub> H <sub>30</sub> Sn <sub>4</sub>	Decamethyltetratin	—	209
C <sub>16</sub> H <sub>40</sub> Cl <sub>2</sub> Sn <sub>4</sub>	1,4-Dichlorooctaethyltetratin	179°–182°	212
C <sub>20</sub> H <sub>50</sub> Sn <sub>4</sub>	Decaethyltetratin	$n_D^{20}$ 1.6283	235d
C <sub>24</sub> H <sub>50</sub> Sn <sub>4</sub>	Phenyltris(triethylstannyl)tin	$n_D^{20}$ 1.6648	235b
C <sub>32</sub> H <sub>72</sub> Sn <sub>4</sub>	Octa- <i>tert</i> -butylcyclotetratin	205° (dec)	225

C <sub>32</sub> H <sub>72</sub> I <sub>2</sub> Sn <sub>4</sub>	1,4-Diiodoocta- <i>tert</i> -butyltetra- <i>n</i> -tin	160°	225
C <sub>36</sub> H <sub>50</sub> Sn <sub>4</sub>	Hexaethyl-2,2,3,3-tetraphenyltetra- <i>n</i> -tin	$n_D^{20}$ 1.6877	235d
C <sub>40</sub> H <sub>90</sub> Sn <sub>4</sub>	Deca- <i>n</i> -butyltetra- <i>n</i> -tin	$n_D^{20}$ 1.5543	235d
C <sub>44</sub> H <sub>82</sub> Sn <sub>4</sub>	2,2-Diphenylocta- <i>n</i> -butyltetra- <i>n</i> -tin	$n_D^{20}$ 1.6085	235d
C <sub>56</sub> H <sub>56</sub> Sn <sub>4</sub>	Octabenzylcyclotetra- <i>n</i> -tin	226°–228° (dec)	236c
C <sub>78</sub> H <sub>161</sub> Sn <sub>4</sub>	Phenyltris(tri- <i>n</i> -octylstannyl)tin	$n_D^{20}$ 1.5345	235b
C <sub>12</sub> H <sub>36</sub> Sn <sub>5</sub>	Dodecamethylpenta- <i>n</i> -tin	—	191
C <sub>24</sub> H <sub>60</sub> Sn <sub>5</sub>	Dodecaethylpenta- <i>n</i> -tin	$n_D^{20}$ 1.6433	235d
C <sub>40</sub> H <sub>90</sub> Cl <sub>2</sub> Sn <sub>5</sub>	1,5-Dichlorodeca- <i>n</i> -butylpenta- <i>n</i> -tin	165°–166°	212
C <sub>60</sub> H <sub>50</sub> Sn <sub>5</sub>	Decaphenylcyclopenta- <i>n</i> -tin	185° (dec)	194a, 236
C <sub>72</sub> H <sub>60</sub> Sn <sub>5</sub>	Tetrakis(triphenylstannyl)tin	280° (dec)	15, 189, 190, 200a
C <sub>12</sub> H <sub>36</sub> Sn <sub>6</sub>	Dodecamethylcyclohexa- <i>n</i> -tin	—	211 <sup>b</sup>
C <sub>24</sub> H <sub>60</sub> Sn <sub>6</sub>	Dodecaethylcyclohexa- <i>n</i> -tin	—	188 <sup>b</sup>
C <sub>28</sub> H <sub>70</sub> Sn <sub>6</sub>	Tetradecaethylhexa- <i>n</i> -tin	$n_D^{20}$ 1.678	235d
C <sub>45</sub> H <sub>108</sub> Sn <sub>6</sub>	Dodecaisobutylcyclohexa- <i>n</i> -tin	—	159
C <sub>72</sub> H <sub>60</sub> Sn <sub>6</sub>	Dodecaphenylcyclohexa- <i>n</i> -tin	270° (dec)	194a, 236, 247
C <sub>72</sub> H <sub>62</sub> Sn <sub>6</sub>	1 <i>H</i> ,6 <i>H</i> -Dodecaphenylhexa- <i>n</i> -tin	—	194a, 236
C <sub>84</sub> H <sub>84</sub> Sn <sub>6</sub>	Dodeca- <i>p</i> -tolylcyclohexa- <i>n</i> -tin	260°–270° (dec)	236b
C <sub>96</sub> H <sub>108</sub> O <sub>12</sub> Sn <sub>6</sub>	Dodeca- <i>p</i> -ethoxyphenylcyclohexa- <i>n</i> -tin	235°–240° (dec)	236b
C <sub>120</sub> H <sub>84</sub> Sn <sub>6</sub>	Dodeca- $\beta$ -naphthylcyclohexa- <i>n</i> -tin	270 (dec)	159, 236b
C <sub>28</sub> H <sub>70</sub> Sn <sub>7</sub>	Tetradecaethylcyclohepta- <i>n</i> -tin	—	188, 192
C <sub>64</sub> H <sub>144</sub> Sn <sub>8</sub>	Hexadeca- <i>n</i> -butylcycloocta- <i>n</i> -tin	—	224 <sup>c</sup>
C <sub>36</sub> H <sub>90</sub> Sn <sub>9</sub>	Octadecaethylcyclonona- <i>n</i> -tin	—	159, 188
C <sub>40</sub> H <sub>100</sub> Sn <sub>10</sub>	Eicosaethylcyclodeca- <i>n</i> -tin	—	224 <sup>c</sup>

<sup>a</sup> Boiling point values are given in parentheses.

<sup>b</sup> Compound not isolated in pure form.

<sup>c</sup> Tentative structure.

dissociation does, in fact, occur in solution. Indeed, 1,1,1-triethyltrimethylditin has been shown to be free of dissociation when heated to 170°C for several hours. At 190°C general decomposition takes place (252a). A tin-tin bond energy of 50 kcal mole<sup>-1</sup> has been calculated for hexaethylditin on the basis of its heat of reaction with benzoyl peroxide (253).

Molar refractions for compounds containing a tin-tin bond have been calculated (254-256). The most recent work shows a tin-tin bond refraction of 10.683 (254).

The Raman spectrum of hexamethylditin has been determined and analyzed, with a tin-tin bond stretching force constant of  $1.0 \pm 0.1 \times 10^5$  dynes cm<sup>-1</sup> calculated (104). The value is smaller than that determined for the silicon-silicon and germanium-germanium bonds in the analogous methyl derivatives. The infrared spectra of hexaphenyl- (257, 258) and hexaethylditin (259, 260) appear in the literature, as well as hexaphenylditin in the 15-35  $\mu$  region (93).

The nuclear magnetic resonance spectrum of hexamethylditin has been determined and compared with that for tetramethyltin (79). A decrease in diamagnetic shielding is observed in the ditin. The NMR spectrum of the same ditin has also been compared with those of octamethyltritin, dodecamethylcyclohexatin, and a dimethyltin polymer of uncertain composition (211). The values of the coupling constant,  $J_{\text{Sn}-\text{CH}_3}$ , were determined and related to the per cent *s* character in the Sn-C bonds. The latter value becomes lower with increasing chain length; consequently, the per cent *s* character in the Sn-Sn bond increases with chain length. The coupling constants are also linearly related to the observed Sn-C stretching frequencies in the infrared spectra of the compounds (211). Still another NMR study involving hexamethylditin and 1,1,1-triethyltrimethylditin has found  $J_{\text{Sn}^{\text{III}}-\text{CH}_3}$  to be anomalously low for the ditin compounds compared with other methyltin derivatives (261, 262).

The ultraviolet spectrum of hexaphenylditin has been determined (92), and it is proposed that there is intense interaction of phenyl groups on opposite tin atoms. The phenomenon, which occurs with analogous compounds of Si, Ge, and Pb, has been attributed in the case of silicon (119) to an excitation involving the silicon-silicon bond. The same explanation is applicable in the case of the tin-tin bond (262a). Ultraviolet spectra of hexaethylditin (250) and octadecaethylcyclononatin (188) have been reported, but without extinction coefficients. The spectra of the perphenylated cyclostannanes have also been discussed (194a). The ultraviolet

absorption of diethyltin (from pyrolysis of the ditin, degree of polymerization not known) is thought to occur at a higher wavelength than hexaethyltin (250). These examples are consistent with the observations for polysilanes (118, 119), but the data are as yet rather sketchy.

## D. Chemical Properties

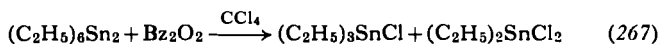
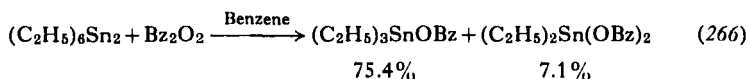
### 1. Cleavage of the Tin-Tin Bond

a. *Electrophilic and Oxidative.* Organopolytin compounds with reactive functional groups attached to tin have been prepared only recently, so that most of the known chemistry of the polytins involves scission of the tin-tin bond. Such cleavage occurs under a variety of oxidative conditions. Some alkyl-substituted ditins are oxidized even in air. Hexamethylditin (206) and hexaethyltin (251) are both unstable in the presence of air, while 1,1,1-trimethyltriphenylditin is unaffected by air (207), and hexaphenylditin in benzene solution withstands treatment with oxygen itself (199). The air oxidation of hexaethyltin in *n*-nonane is proposed to occur through the initial formation of the peroxide,  $[(C_2H_5)_3SnO]_2$ , which is subsequently converted to bis(triethyltin) oxide (259). The recently prepared 1*H*,2*H*-tetra-*n*-butylditin reacts with air to form dibutyltin oxide (243). 1,2-Diacet-oxytetra-*n*-butylditin also decomposes slowly in air, while the analogous tetraphenyl compound is unaffected over 48 days (240, 241). The reaction of hexaethyltin with oxygen has been studied by Harada (210) and by Aleksandrov and co-workers (263, 264). The products obtained under the conditions of the latter workers are bis(triethyltin) oxide and diethyltin oxide, and a free radical chain mechanism is involved. Elemental sulfur has been shown to react with hexamethylditin in benzene to form bis(trimethyltin) sulfide (206).

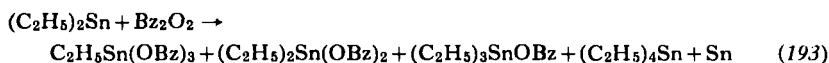
Reaction with alcoholic silver nitrate has been used as a qualitative test for the ditin linkage, and a variety of compounds, including aryl derivatives, have been shown to deposit a silver mirror on treatment with the reagent (195, 198, 200, 215, 244). Potassium permanganate is also reduced readily (200, 265). Hexaphenylditin has been shown to react virtually quantitatively to produce triphenyltin hydroxide when subjected to the action of potassium permanganate in acetone solution (265).

A variety of other oxidizing agents, including dibenzoyl peroxide (253, 266, 267), acetyl benzoyl peroxide (266), di-*tert*-butyl peroxide (141),

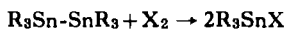
cyclohexyl percarbonate (266), lead tetraacetate (266), and nitrosoacetanilide (266, 268, 269) have been shown to cleave the tin-tin bond homolytically.



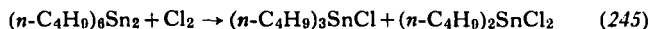
Although the reaction with benzoyl peroxide apparently results in some cleavage of ethyl groups from tin, it has been exploited for the structural investigation of some diorganotin polymers (193, 194, 228, 270). A polymer produced from hexaethylditin and aluminum chloride was treated with the peroxide to show that the tin chains contained considerable branching.



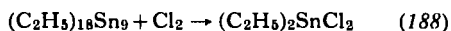
The most thoroughly examined reaction of the tin-tin bond is that with the halogens.



The reactions with bromine (192, 195, 198, 200, 224, 240, 241, 271, 272) and iodine (188, 189, 192, 197, 198, 200, 206, 213, 214, 236, 244, 265, 271) are believed to be quantitative and have been employed for the analysis of ditin content. Reaction with chlorine in some cases results in cleavage of organic groups from tin as well as the expected tin-tin scission (244, 245).



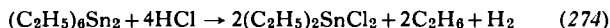
No ditin has been observed to be resistant to halogen cleavage. Even a compound such as hexakis(2-biphenyl)ditin, which could be expected to exhibit considerable steric hindrance to reaction, readily decolorizes bromine in carbon tetrachloride and iodine in benzene (200). The reaction has a number of potentialities for structural analysis. As an example, the compounds recently prepared by Neumann from diorganotin dihydrides and basic reagents were shown to have a cyclic structure by use of the reactions with chlorine, bromine, or iodine (188, 192, 236). The compounds gave only diorganotin dihalides after halogen cleavage with no triorganotin halide or organotin trihalide being isolated.



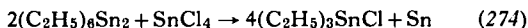
A dibutyltin polymer prepared from *n*-butyllithium and stannous chloride

likewise showed specific cleavage to dibutyltin dibromide on treatment with bromine (224).

Cleavage with formation of the halide is accomplished with a number of reagents other than the halogens. Treatment of hexamethylditin with hydrobromic (206) or hydrochloric (273) acid leads to the corresponding trimethyltin halide. In contrast, hexaethylditin has been found to react with 4 moles of hydrogen chloride to form diethyltin dichloride.

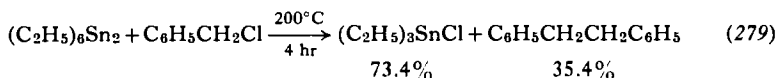


Mercuric chloride has been used by several workers to obtain the triorganotin halide (200, 202, 203, 206, 275), and stannic chloride in greater than catalytic amounts is also effective.

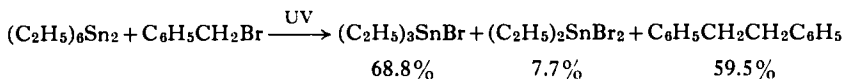


Gold trichloride has recently been shown to react with hexamethylditin to produce dimethyltin dichloride as well as trimethyltin chloride (273).

An interesting reaction that has been proposed (276) to have a free radical mechanism is the interaction of hexamethylditin and trifluoroiodomethane, catalyzed by ultraviolet light. The product isolated is trifluoromethyltrimethyltin (276, 277). The same reaction occurs under the influence of heat, but a cyclic mechanism is favored for this process (278). A variety of organic halides have been shown to react with hexaethylditin (275, 279, 280). Temperatures above 100° C are usually required in order to bring about reaction in a reasonable length of time.



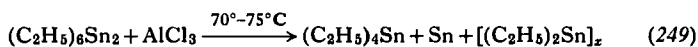
Ultraviolet light also catalyzes the reaction of hexaethylditin with benzyl bromide (281).



As has been indicated earlier, an organic halide such as carbon tetrachloride can react with a ditin to produce the triorganotin halide with the aid of a free radical initiator such as benzoyl peroxide (266, 267). Again with ultraviolet catalysis, hexamethylditin adds to tetrafluoroethylene to produce 1,2-bis-(trimethylstannyl)tetrafluoroethane (282). A similar reaction occurs with perfluoropropylene (282a).



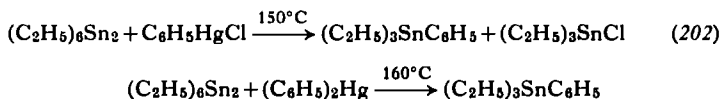
A number of Lewis acids have been shown to effect disproportionation of hexaorganoditin compounds. Treatment of hexaethylditin with aluminum chloride in catalytic amounts results in the formation of tetraethyltin, metallic tin, and a diethyltin polymer.



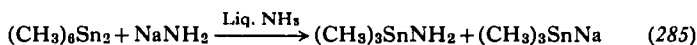
The reaction does not occur with tetraethyltin even under more forcing conditions, so that it has been proposed as a qualitative test for the tin-tin linkage (141). The same type of process also occurs with aluminum bromide (270), stannous chloride (270), and zirconium (250), titanium (250), and tin (250, 270) tetrachlorides.

In the presence of isopropyl bromide, aluminum chloride reacts with hexaethylditin to produce triethyltin bromide in addition to tetraethyltin (283). Boron trifluoride, dimethylboron fluoride, and diborane have also been shown to bring about the cleavage of hexamethylditin to form tetramethyltin (284).

b. *Nucleophilic and Reductive.* As would be expected by analogy with other Group IVB elements, the tin-tin bond is susceptible to attack by nucleophilic reagents. Hexaphenylditin is not affected by hot alcoholic potassium hydroxide, but lack of solubility is probably a significant hindrance to this reaction (85a). The compound is cleaved by hot moist piperidine to produce bis(triphenyltin) oxide, and the reaction mixture is a homogeneous one (85a). Hexa-*n*-butyl- and hexaphenylditin are cleaved by lithium aluminum hydride, but the reactions lead to a rather complex product mixture and are not very facile (246). Phenyllithium cleaves hexaphenylditin to give tetraphenyltin in 88.6% yield (221). Phenylmercuric chloride and diphenylmercury have been shown to produce a similar cleavage (202, 203).

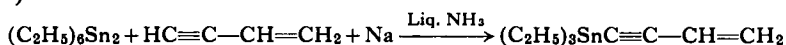


Sodium amide in liquid ammonia is also effective.



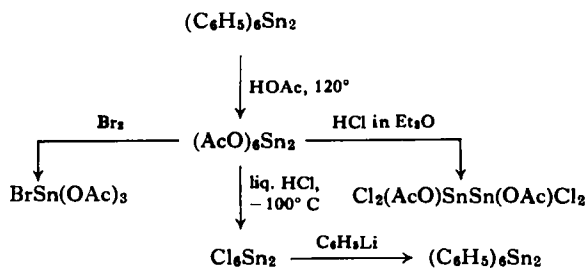
On the other hand, the monosodium adduct of naphthalene leads to reduction of hexaphenylditin with formation of triphenyltinsodium (252).

Alkali metals themselves also produce this reduction. The earliest system used was sodium in liquid ammonia (206, 208, 215), with which Kraus prepared trimethyltinsodium from hexamethylditin (206). Sodium-potassium alloy in ethylene glycol dimethyl ether also cleaves the same ditin (38). Most recently, lithium in tetrahydrofuran has been shown to cleave hexaphenylditin (218, 219) and hexa-*n*-butylditin (220). Also, hexaphenylditin may be cleaved by magnesium in tetrahydrofuran when the reaction is initiated by ethyl bromide (286). In an interesting variation, a catalytic amount of sodium in liquid ammonia causes the addition of vinylacetylene to hexaethylditin (287).



## 2. Reactions without Tin-Tin Bond Cleavage

Relatively few reactions of polytin compounds are known to proceed without cleavage of the tin-tin bond. Some of these reactions (243) are discussed in the section on methods of preparation. Quite recently it has been observed that hexaphenylditin reacts with glacial acetic acid to produce hexaacetoxyditin, a very stable compound which may be converted to other ditin derivatives (288).



V

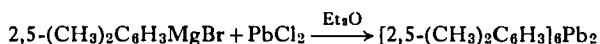
## LEAD

### A. Historical

The synthesis of the first organodilead compound was claimed in 1853 by Löwig (289), who reported the preparation of hexaethyldilead by the reaction of ethyl iodide with a sodium-lead alloy. Löwig described this compound as a heavy, fairly stable liquid, containing only lead, carbon, and hydrogen. Since the formulas given by Löwig are antiquated and the atomic weight

of lead was considered to be 103, it is impossible to ascertain whether he assumed the formula for his compound as  $\text{Pb}(\text{C}_2\text{H}_5)_3$  or  $\text{Pb}_2(\text{C}_2\text{H}_5)_6$ . In addition, neither a molecular weight determination nor a lead analysis accompanied his work. Several years later, work by Buckton (290) indicated that the compound obtained by Löwig was probably impure tetraethyllead. This latter conclusion was substantiated by Ghira (291) who repeated Löwig's work and definitely established that the product previously described as hexaethyllead, was actually tetraethyllead. At that time (1894) Ghira stated, "I think it is not too much to presume that at the present time no lead compounds of the type  $\text{PbX}_3$  or  $\text{Pb}_2\text{X}_6$  have ever been reported, studied or isolated."

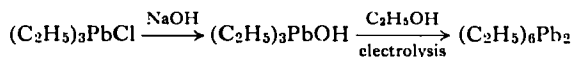
The first authentic preparation of a dilead compound, namely, hexa-*p*-xylyldilead, was reported in 1919 by Krause and Schmitz (292). Their preparation was accomplished by the reaction of *p*-xylylmagnesium bromide with lead dichloride.



This dilead compound was described as a pale greenish yellow powder which sintered at  $220^\circ\text{C}$  (incipient decomposition) and melted with blackening at  $225^\circ\text{C}$ .

In 1921, Krause (293) similarly prepared hexacyclohexyldilead, the first reported hexaalkyldilead. During the course of his investigation, however, Krause expressed the opinion that his evidence indicated that the compound prepared in 1914 by Grüttner (294), and described at that time as tetra-cyclohexyllead, was probably impure hexacyclohexyldilead.

It was not until 1923 that the first well-documented preparation of hexaethyllead was reported by Midgley and co-workers (295). The procedure employed by these workers involved the electrolysis of triethyllead hydroxide using a lead electrode.



Hexaethyllead was described as a yellow oil (b.p. approximately  $100^\circ\text{C}/2\text{ mm}$ ) which does not freeze even at  $-80^\circ\text{C}$ , decomposes easily in air and also when distilled directly.

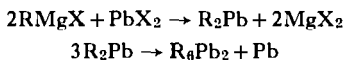
The (1) color, (2) unusual melting point characteristics, (3) facile formation of pale yellow solutions (in organic solvents) which were rapidly decolorized in the presence of sunlight, (4) variation of molecular weights

with concentration, and (5) the ease of cleavage of the Pb—Pb bond by halogens were indications of the unusual properties to be expected for other dilead compounds.

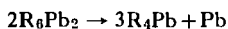
The most highly catenated lead compound reported (15, 295*a*), namely, tetrakis(triphenylplumbyl)lead, exhibits the properties predicted by the first dilead compounds prepared. This tetrakis compound is a bright red solid which decomposes to hexaphenyldilead and lead (oxide) simply upon standing. Reaction with iodine gives almost exclusively triphenyllead iodide and lead diiodide.

### B. Preparation

The method most often employed for the preparation of  $R_6Pb_2$  compounds is that involving the reaction of  $PbCl_2$  with the appropriate Grignard reagent. These reactions proceed with initial formation of highly unstable  $R_2Pb$  derivatives followed by spontaneous disproportionation to the desired  $R_6Pb_2$ .



With the smaller R groups (methyl, ethyl, etc.) careful control of the reaction conditions is necessary to prevent further disproportionation of  $R_6Pb_2$  to  $R_4Pb$ .



To illustrate the value and versatility of this synthetic method, a presentation of the  $R_6Pb_2$  compounds prepared by this procedure is given in Table IV (296, 297, etc.).

Examination of Table IV shows that while this method has been used most extensively for the preparation of hexaaryldileads, equally good results can be obtained with several hexaalkyldileads. However, the hexaalkyldilead compounds prepared by this method are usually contaminated with the corresponding  $R_4Pb$  derivative, and the difficulties involved in the distillation of the hexaalkyldileads makes separation nearly impossible. With the aryl derivatives, solid products are obtained and hexaaryldileads may be obtained in a pure state by fractional crystallization.

A variation of the above method involves the reaction of  $PbCl_2$  with the organolithium reagent. This variation has been successful in the synthesis of hexaphenyldilead (172, 296, 298, 299) and hexa-1-naphthyldilead (296).

TABLE IV  
 HEXAORGANODILEADS PREPARED FROM RMgX AND PbCl<sub>2</sub>

R in R <sub>6</sub> Pb <sub>2</sub>	Reference [yield, %]
Methyl	302 <sup>a</sup> , 304 [61], 305 <sup>a</sup>
Cyclohexyl	293 [50], 296 [64]
β-Phenethyl	306 <sup>a</sup>
Phenyl	296 [21–25], 307 [40], 308 <sup>a</sup> , 309 <sup>a</sup> , 310 <sup>a</sup>
<i>o</i> -Tolyl	307 [50], 311 [51]
<i>m</i> -Tolyl	296 <sup>a</sup>
<i>p</i> -Tolyl	296 [44], 307 [45–50]
<i>o</i> -Methoxyphenyl	296 [59], 312 [59]
<i>p</i> -Methoxyphenyl	296 [57.1], 312 [57.1], 313 [65.4]
<i>o</i> -Ethoxyphenyl	296 [23.4], 312 [23.4]
<i>p</i> -Ethoxyphenyl	296 [58.4], 312 [58.4]
<i>m</i> -Xylyl	314 <sup>a</sup>
<i>p</i> -Xylyl	292 [50], 315 <sup>a</sup>
Mesityl	296 <sup>a</sup> , 312 <sup>a</sup> , 316 <sup>a</sup>
<i>o</i> -Bromobenzyl	317 [14]
<i>o</i> -Chlorobenzyl	317 [22]
1-Naphthyl	296 [6–10], 312 [6–10]

<sup>a</sup> Yield not given.

Another reaction commonly employed for the preparation of R<sub>6</sub>Pb<sub>2</sub> derivatives involves the coupling of R<sub>3</sub>PbX compounds with sodium in liquid ammonia. The compounds prepared by this method are listed in

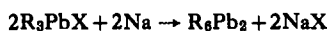


Table V. Although examination of Table V shows that this method has been used less often than the RMgX–PbCl<sub>2</sub> method, excellent yields of the desired dilead compounds were obtained in most cases. In addition, this method is extremely useful for the preparation of pure hexaalkyldileads.

The coupling of diorganolead dihalides with lithium and calcium has also been reported (300, 301) as well as that of triphenyllead chloride with tetrasodium nonaplumbide [Na<sub>4</sub>Pb<sub>9</sub>] (297).

A third method employed for the synthesis of R<sub>6</sub>Pb<sub>2</sub> compounds involves the basic hydrolysis and electrolysis of R<sub>3</sub>PbX using a lead electrode. The first hexaalkyldilead (hexaethyldilead) was prepared by this method (295, 302, 303).

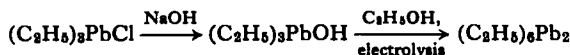


TABLE V  
HEXAORGANODILEADS PREPARED FROM  $R_3PbX$  AND  
 $Na/Liq. NH_3$

R in $R_6Pb_2$	Reference [yield, %]
Methyl	304 [7]
Ethyl	296 [69], 318 [approx. 100]
Phenyl	296 [94], 297 [90]
<i>m</i> -Tolyl	296 [70]

A modification of this method has been used by Hein and Klein (319) for the synthesis of hexamethyl- and hexaethyldilead in good to excellent yields. A recent report (320), however, states that this modified method (319) gives mixtures of  $(C_2H_5)_2Pb$  and  $(C_2H_5)_6Pb_2$ . No reports concerning the preparation of hexaaryldileads by the electrolytic method have appeared, presumably because the aryl derivatives are readily obtainable by other procedures.

In addition to the above general methods, polylead derivatives have been obtained as reaction products in the following cases:

- tetrakis(triphenylplumbyl)lead, from the simultaneous hydrolysis and oxidation of triphenyllead-lithium (or diphenyllead) in the cold by a hydrogen peroxide-ice-salt mixture (321);
- hexaphenyldilead, from the air hydrolysis of triphenyllead-lithium ( $PbBr_2 + C_6H_5Li$ ) (322);
- hexaphenyldilead, from triphenyllead-sodium and 1,2-dibromoethane (323);
- hexacyclohexyldilead, from tricyclohexyllead-sodium and mercury (324);
- hexaisopropyldilead, from acetone and sodium-lead alloy in sulfuric acid (325);
- hexamethyldilead, from the thermal decomposition of trimethyllead hydride  $(CH_3)_3PbH$  (326);
- hexamethyldilead, from trimethyllead chloride and  $NH_4[Pb(CH_3)_3]$  [prepared from  $(CH_3)_3PbH$  and liquid  $NH_3$ ] (327).

To date, only  $R_6Pb_2$  compounds in which all R groups are identical are known, although an unsuccessful attempt to prepare *sym*-diphenyltetracyclohexyl- and *sym*-diethyltetraphenyldilead, by sodium coupling of the

TABLE VI  
 ORGANOPOLYLEADS

Formula	R in R <sub>6</sub> Pb <sub>2</sub>	Properties	References
C <sub>6</sub> H <sub>18</sub> Pb <sub>2</sub>	Methyl	Yellow solid, m.p. 38° C; fairly unstable	304
C <sub>12</sub> H <sub>30</sub> Pb <sub>2</sub>	Ethyl	Yellow oil, b.p. 100° C/2 mm; easily decomposed by air	295, 318
C <sub>18</sub> H <sub>42</sub> Pb <sub>2</sub>	<i>n</i> -Propyl	—	328 <sup>a</sup>
C <sub>18</sub> H <sub>42</sub> Pb <sub>2</sub>	Isopropyl	—	325 <sup>b</sup>
C <sub>24</sub> H <sub>54</sub> Pb <sub>2</sub>	<i>n</i> -Butyl	—	329 <sup>b</sup> , 330 <sup>b</sup>
C <sub>36</sub> H <sub>30</sub> Pb <sub>2</sub>	Phenyl	Light yellow solid, m.p. 155°–160° C; deposits lead at 225° C	296–298, 307
C <sub>36</sub> H <sub>66</sub> Pb <sub>2</sub>	Cyclohexyl	Yellow solid, m.p. 190° C (dec); sensitive to light	293, 296
C <sub>42</sub> H <sub>36</sub> Br <sub>6</sub> Pb <sub>2</sub>	<i>o</i> -Bromobenzyl	Deep red solid, dec 170° C	317
C <sub>42</sub> H <sub>36</sub> Cl <sub>6</sub> Pb <sub>2</sub>	<i>o</i> -Chlorobenzyl	Light red solid, dec 170° C	317
C <sub>42</sub> H <sub>42</sub> Pb <sub>2</sub>	<i>o</i> -Tolyl	dec 240° C	307
C <sub>42</sub> H <sub>42</sub> Pb <sub>2</sub>	<i>m</i> -Tolyl	M.p. 104° C (dec 116°–117° C)	296, 312
C <sub>42</sub> H <sub>42</sub> Pb <sub>2</sub>	<i>p</i> -Tolyl	dec 193° C	296, 307, 312
C <sub>42</sub> H <sub>42</sub> O <sub>6</sub> Pb <sub>2</sub>	<i>o</i> -Methoxyphenyl	M.p. 198°–201°	296, 312
C <sub>42</sub> H <sub>42</sub> O <sub>6</sub> Pb <sub>2</sub>	<i>p</i> -Methoxyphenyl	M.p. 198°–200°	296, 312
C <sub>48</sub> H <sub>54</sub> Pb <sub>2</sub>	<i>m</i> -Xylyl	Pale yellow solid, m.p. 233.5° C (dec)	314
C <sub>48</sub> H <sub>54</sub> Pb <sub>2</sub>	<i>p</i> -Xylyl	Greenish yellow solid, m.p. 220° C (dec)	292, 315
C <sub>48</sub> H <sub>54</sub> Pb <sub>2</sub>	$\beta$ -Phenethyl	—	306 <sup>a</sup>
C <sub>48</sub> H <sub>60</sub> O <sub>6</sub> Pb <sub>2</sub>	<i>o</i> -Ethoxyphenyl	M.p. 170°–171° C (dec)	296, 312
C <sub>48</sub> H <sub>60</sub> O <sub>6</sub> Pb <sub>2</sub>	<i>p</i> -Ethoxyphenyl	M.p. 178°–179° C (dec)	296, 312
C <sub>54</sub> H <sub>66</sub> Pb <sub>2</sub>	Mesityl	M.p. 325° C	296, 312
C <sub>60</sub> H <sub>42</sub> Pb <sub>2</sub>	1-Naphthyl	M.p. 255° C (dec)	296, 312
<i>Pentalead</i>			
Formula	Compound	Properties	References
C <sub>72</sub> H <sub>60</sub> Pb <sub>5</sub>	Tetrakis (tri-phenylplumbyl)-lead	Red solid, slowly decomposes on standing	15, 321

<sup>a</sup> Properties not reported.<sup>b</sup> Compound not isolated.

corresponding triorganolead halides, has been reported (300). It has been suggested that the unsymmetrical compounds may be unstable, rapidly disproportionating into the symmetrical hexaalkyl or hexaaryldilead (15).

For reference purposes, a tabulation of the reported polylead compounds is given in Table VI.

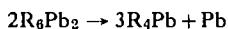
### C. Physical Properties

#### 1. Thermal Stability

Hexaorganodileads are in general colored compounds which exhibit moderate to poor thermal stability. The alkyl derivatives are liquids or low-melting solids which are quite unstable and difficult to purify since they decompose during distillation. The aryl derivatives are crystalline solids which are considerably more stable and readily purified by recrystallization. They exhibit good solubility in benzene and chloroform, moderate solubility in acetone and ether, and insolubility in alcohol, petroleum ether, or water. In the solid state and protected from strong light, these aryl derivatives are stable for long periods.

Hexacyclohexyldilead plays a dual role. Although it is a hexaalkyldilead, it is a high-melting solid with a stability similar to that of the hexaaryldileads.

A characteristic common to all  $R_6Pb_2$  compounds is their thermal disproportionation to the corresponding  $R_4Pb$  compound and metallic lead. The temperature required for this decomposition depends on the nature of



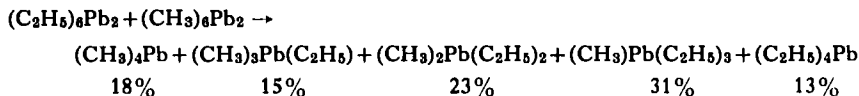
the R groups. The hexaalkyl (302) compounds decompose upon distillation, whereas the hexaaryl (307) derivatives decompose at or before melting (the resulting residue then melts at the melting point of the corresponding  $R_4Pb$  compound).

The disproportionation is also observed in high-boiling solvents (toluene, xylene, pyridine) and the order of decreasing ease of pyrolysis of the  $R_6Pb_2$  compounds has been reported (296) to be: ethyl, methyl > *m*-tolyl, phenyl > *p*-tolyl, *p*-ethoxyphenyl, *p*-methoxyphenyl > *o*-tolyl, *o*-ethoxyphenyl, *o*-methoxyphenyl > cyclohexyl, mesityl, 1-naphthyl.

The decomposition of  $R_6Pb_2$  to  $R_4Pb$  has been observed using activated carbon black (331), silica-type catalysts (332), aluminum chloride (249), and ultraviolet light (333). Autocatalysis by metallic lead, though less effective, has also been reported (334).

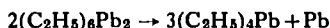


The yields of  $R_4Pb$  obtained from these disproportionation reactions are generally quite high [90%] (296). In accord with the stoichiometry illustrated in the above equation, Calingaert, Soroos, and Shapiro (302) heated a mixture of hexamethyl- and hexaethyldilead under nitrogen at 100° C and obtained metallic lead in an amount within 5% of the theoretical. In addition, all possible  $R_4Pb$  compounds were formed.



Recently, tetrakis(triphenylplumbyl)lead,  $[(C_6H_5)_3Pb]_4Pb$ , has been reported (15, 321) to disproportionate slowly (simply upon standing) to hexaphenyldilead and lead (oxide).

While the mechanism of these disproportionations is not clear, recent reports indicate that considerable progress is being made toward a more complete understanding of this problem. In the case of hexaethyldilead, Razuvaev and co-workers have suggested that in addition to the disproportionation reaction generally accepted,



an additional mode of decomposition is operative (249, 308, 335).



The first reaction is strongly catalyzed by aluminum chloride (249). The second reaction is induced thermally and also autocatalyzed by the metallic lead formed, and accounts for the formation of gaseous products (ethane, ethylene, butane) during the decomposition (249, 336).

Recent studies on the decomposition of hexaphenyldilead have given evidence for the following equilibrium:



Such studies include the decomposition of hexaphenyldilead (a) in various solvents in the presence of metal salts (337); (b) in refluxing acetic acid (308); and (c) tagged with radium D, a radioactive lead isotope, in benzene solvent in the presence of tetraphenyllead (338).

At the present time, experimental data (249, 308, 336, 337, 339) are consistent with the decomposition of  $R_6Pb_2$  to  $R_4Pb$  and elemental lead *via* the unstable  $R_2Pb$  intermediate.

## 2. Spectral

The infrared spectrum of hexaphenyldilead has been determined (93) in connection with a study of the spectral properties of the phenyl compounds of Groups IVB, VB, and VIIB. The infrared and Raman spectra of hexaethyllead have been compared to those of tetraethyllead (340).

The ultraviolet spectrum of hexacyclohexyldilead (in benzene) has been reported (341) to show no maxima in either the visible or the ultraviolet region. Recently, Hague and Prince (92) have reported that hexaphenyldilead (in cyclohexane) shows intense absorption bands at 245 (shoulder,  $\epsilon = 33,900$ ) and 293 ( $\epsilon = 35,000$ )  $m\mu$ . These spectral properties suggested an intense interaction between phenyl groups on different lead atoms through the Pb—Pb bond (92). Further, this unusual type of conjugation was considered to occur through overlap of suitable vacant *d*- orbitals on the lead atom. A reexamination of the ultraviolet spectrum of hexacyclohexyldilead (in cyclohexane) showed the presence of intense absorption bands at 250 and 289  $m\mu$  (89) (i.e., somewhat similar to that of hexaphenyldilead). Recently, the thermochromic behavior of hexacyclohexyldilead, as well as of hexaphenyldilead has been studied (341a). This study demonstrated that the color of these lead compounds is not due to the presence of free radicals. In view of these latter reinvestigations (89, 341a), and recent work on the ultraviolet properties of alkyl polysilanes (118, 119), it is apparent that the interpretation proposed by Hague and Prince is inadequate. The ultraviolet absorption bands appear to be characteristic of the Pb—Pb bond. Recently, the ultraviolet spectrum of tetrakis(triphenylplumbyl)lead has been reported (15, 262a), and the absorption in the 220–700  $m\mu$  region was also attributed to the metal–metal system.

## 3. Bond Length

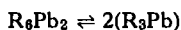
An electron diffraction study of the molecular structure of hexamethyldilead has been carried out (305). The Pb—Pb distance was found to be equal to  $2.88 \pm 0.03$  Å and the Pb—C distances equal to  $2.25 \pm 0.06$  Å, indicating nothing unexpected in the structure. These results gave a normal covalent radius of lead equal to  $1.44 \pm 0.02$  Å.

An X-ray analysis of hexaphenyldilead has recently been reported (15, 342). In this study two different values were obtained for the Pb—Pb distance, namely,  $2.94 \pm 0.09$  Å and  $2.75 \pm 0.09$  Å. In an attempt to explain

this unexpected result, the presence of an ionic lattice consisting of  $(C_6H_5)_2Pb^{2+}$  ions and dimeric  $(C_6H_5)_4Pb^{2-}$  ions was assumed. No previous suggestions of ionic structures for dilead compounds have been reported. No data are available on the bond energy of the Pb—Pb linkage in hexaorganodileads.

#### 4. Dissociation

Since the initial preparation of dileads, a considerable amount of work has been reported concerning the possible dissociation of these compounds in solution. Subsequent to the preparation of hexa-*p*-xylyldilead, Krause (292)



observed that this compound formed yellow solutions in organic solvents which were quickly decolorized by sunlight, depositing a white solid. While molecular weight determinations favored the dimeric species ( $R_6Pb_2$ ), Krause suggested that the yellow color was indicative of dissociation by light. Several years later, Krause (293) prepared hexacyclohexyldilead and noted that this compound was readily decomposed by light, but quite stable in the dark. He also reported that the molecular weight varied with concentration. Similar molecular weight variations were observed with hexaphenyldilead (297, 307) and hexa-*p*-tolylldilead (307). Also, molecular weight results presented by Midgley and associates (295) indicated that hexaethyldilead was dissociated into  $(C_2H_5)_3Pb$  in dilute solutions, but that the dimeric form existed at higher concentrations.

In view of the early molecular weight results indicating dissociation in dilute solutions, the slight color present in  $R_6Pb_2$  compounds, and the formal analogy of  $R_6Pb_2$  compounds with hexaarylethanes, it is not surprising that Krause (343) considered these compounds to be triorganolead derivatives. Indeed they are often designated as such in the older literature.

Since the above reports, molecular weight determinations on hexaphenyldilead (309, 344, 345), hexacyclohexyldilead (344) and hexamesityldilead (346) have been reported to favor the dimeric ( $R_6Pb_2$ ) form. The latter reports are in agreement with magnetic susceptibility measurements on hexaphenyldilead (347), hexacyclohexyldilead (348, 349), hexakis(*o*-bromobenzyl)- and hexakis(*o*-chlorobenzyl)dilead (317).

During recent years only one report (316) favors dissociation. This latter report was based on measurements of the freezing point depression of benzene by hexamesityldilead and on measurements of the magnetic

susceptibility. That even this recent report is in error is indicated by recent physical measurements. Thus, other workers (346) have shown by paramagnetic resonance that hexamesityldilead is not dissociated when dissolved in benzene. Also, no exchange has been observed between hexaphenyldilead (tagged with radium D, a radioactive lead isotope) and triphenyllead chloride in benzene (338). Electron spin resonance measurements conducted with chloroform and benzene solutions of hexaphenyldilead, as well as solid hexaphenyldilead, show that this compound does not undergo radical dissociation (338). Even electron spin resonance measurements on an ultraviolet-light-irradiated solution (under nitrogen) of hexaphenyldilead, conditions known (333) to produce elemental lead and tetraphenyllead, do not show the presence of radicals (350).

In an attempt to resolve the two opposing views, some objections have been cited (15) against the cryoscopic method of establishing dissociation. First, in view of the high molecular weights of the dilead compounds, a depression of only a few hundredths of a centigrade degree may be obtained. Second, since  $R_6Pb_2$  compounds are unstable in solution, decomposition products may give rise to too great a depression. Finally, these factors assume greater importance when one remembers that dissociation has been observed only in dilute solutions.

It seems quite apparent that while the low molecular weights and colored solutions indicate decomposition, present evidence argues against the formation, in solution, of stable free radicals.

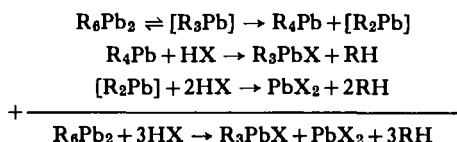
#### D. Chemical Properties

##### 1. *Electrophilic and Oxidative Cleavage of the Lead-Lead Bond*

a. *With Halogens and Hydrogen Halides.* The reaction of hexaorgano-dilead compounds with halogens was first studied by Krause and Schmitz (292). They observed that treatment of hexa-*p*-xylyldilead with bromine in pyridine gave tri-*p*-xylyllead bromide; however, using chloroform as solvent the product obtained was di-*p*-xylyllead dibromide. Shortly thereafter it was reported that hexaphenyl- (307); hexacyclohexyl- (293); and hexa-*p*-tolyllead (307) react with halogens (bromine and iodine) to give good yields of the corresponding triorganolead halides. Since these early reports, the halogenation of hexamesityl- (312); hexacyclohexyl- (312, 324); hexa-*o*-tolyl- (311); hexa- $\beta$ -phenethyl- (306); hexa-*o*-methoxyphenyl- (296); hexa-*p*-methoxyphenyl- (296); hexa-*o*-ethoxyphenyl- (296, 312);

and hexa-*p*-ethoxyphenyldilead (296, 312) has been carried out. Generally, it is difficult to control the halogenation reactions, and the resulting product consists of a mixture of  $R_3PbX$ ,  $R_2PbX_2$ , and  $PbX_2$ , in yields varying with the reactant and reaction conditions employed. Cleavage of the recently reported (15, 321) tetrakis(triphenylplumbyl)lead with iodine produces almost exclusively triphenyllead iodide and lead diiodide, indicating a branched Pb—Pb chain.

The reaction of hexaorganodileads with hydrogen halides has been observed to take place readily at room temperature (295, 296, 311–313, 339, 351). The acid cleavage reactions are more complex since organolead hydrides are apparently not formed. From the products isolated the following series of reactions has been suggested (308, 339):



The above sequence has been used to explain the products obtained from the reaction of hexaorganodileads with hydrogen chloride (339), acetic acid (308), thiolacetic acid (308), sulfur (308), and 1,2-dibromoethane (308).

From an early qualitative investigation concerned with the reaction of hexaethyllead and hydrogen chloride, Midgley, Hochwalt, and Calingaert (295) postulated the reaction, in order to explain the formation of a white



precipitate and a colorless gas. It was stated (351) that while this reaction suggested that hydrogen chloride attacks the Pb—C bond before the Pb—Pb bond, such preferential Pb—C bond cleavages had not been substantiated in the literature. Recent results (351) on the ethanolic hydrogen chloride cleavages of hexaalkyl and hexaaryllead compounds confirm the over-all stoichiometry of the reaction to be that illustrated above. The results are cited (351) as the first proven reactions in which the Pb—C bond is cleaved before the Pb—Pb bond. These results, however, did not show the stage of the reaction at which the lead chloride is formed. Two possibilities were presented (351).

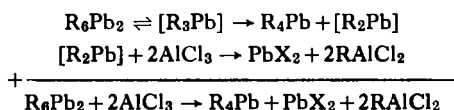


Evidence for the intermediate  $ClR_2PbPbR_2Cl$  [Eq. (7)] was obtained (351) from the reaction of anhydrous aluminum chloride with  $R_6Pb_2$  compounds

[a reaction first investigated with Apperson (349)]. This evidence was the isolation of nearly equal amounts of  $R_4Pb$  and  $PbCl_2$  in accord with the following equation:



While the above reaction schemes explain the results, it is also possible to explain them in terms of the disproportionation of  $R_6Pb_2$  (in solution) *via* the unstable  $R_2Pb$  intermediate previously discussed above (308, 339).

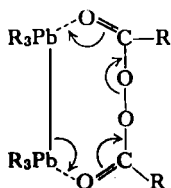


This latter explanation does not necessitate the postulation of either the preferential Pb—C cleavage or the as yet uncharacterized  $ClR_2PbPbR_2Cl$  intermediate. Further work is necessary in order to resolve these conflicting mechanistic interpretations.

b. *With Oxygen and Related Species.* The autoxidation of hexacyclohexyldilead has been studied in some detail by Hein (341). He reports that the reaction was photochemical, occurring only under the influence of ultraviolet light and not at all in the dark or in sodium vapor light. He extended his studies to reactions in the presence of compounds such as carbon tetrachloride or carbon tetrabromide. Indeed, hexacyclohexyldilead has been used for the formation of photosensitive layers (352).

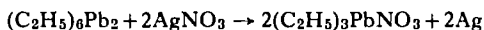
The reaction of hexaethyldilead with oxygen at elevated temperatures has been studied (259, 264, 353). The final products [ $(C_2H_5)_3PbOH$ ,  $C_2H_6$ ,  $C_2H_4$ ,  $PbO$ ] were shown to be formed from the intermediate bis(triethyllead) oxide. The infrared spectrum of this latter compound, a green reactive liquid, was also reported (264, 353).

The reaction of hexaethyldilead with peroxides has been reported (266) to result in cleavage of the Pb—Pb bond. The reaction does not appear to proceed via free radicals since no reaction is obtained with azobis(isobutyronitrile) (AIBN). In view of these latter results with AIBN the reaction was postulated to proceed by homolytic scission of a cyclic intermediate.



The cleavage of hexaethyldilead by aralkyl hydroperoxides has also been studied (354). The initial product of these reactions is  $(C_2H_5)_3PbOH$ . The yield of this compound declines with increasing peroxide concentration. An excess of peroxide gives only  $(C_2H_5)_3PbOR$  and  $(C_2H_5)_3PbOOR$ . Addition of water causes an immediate hydrolysis of these latter compounds.

c. *Miscellaneous.* The reactions of hexaorganodileads with silver salts at low temperatures give green-colored solutions believed to be  $R_3PbAg$  derivatives (343). Recently, this reaction has been studied with hexaethyldilead in ethanolic solutions at room temperature (303, 327). The over-all reaction under these conditions is,



since the intermediate  $R_3PbAg$  compound is not stable under these conditions.

Other heavy metal salts which have been studied are  $HgCl_2$  (355),  $Hg_2Cl_2$  (355),  $AuCl_3$  (355),  $CuCl_2$  (337, 355),  $Cu_2Cl_2$  (355),  $FeCl_3$  (355, 356), and  $TiCl_3$  (314).

Cleavage of hexaorganodileads with potassium permanganate gives the corresponding triorganolead hydroxides (356, 357).

The reactions of hexaorganodileads with nitric acid (358, 359), dimethylacetic acid (358), magnesium/magnesium iodide (296), aluminum chloride (349, 360), and alkyl halides (280, 361, 362) also result in Pb—Pb cleavage. Reaction of hexaethyldilead with sulfuryl chloride, thionyl chloride, sulfur dichloride, and sulfur monochloride has been reported (363). The yield of triethyllead chloride was observed to decrease with increasing nucleophilic character of the sulfur atom, in the order listed above.

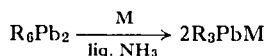
The hydrogenolysis of hexaphenyldilead has been reported (299) to yield elemental lead and either biphenyl or tetraphenyllead depending upon the catalyst and reaction conditions employed.

The reaction of hexaphenyldilead with maleic anhydride has been reported (300, 301) to give an adduct, 2,3-bis(triphenylplumbyl)succinic anhydride. Recently, however, evidence has been set forth that the product probably was diphenyllead maleate (15), formed from maleic acid impurities in the starting anhydride. Support for this conclusion came from the absence of any observable reaction with pure maleic anhydride.

## 2. Nucleophilic and Reductive Cleavage of the Lead-Lead Bond

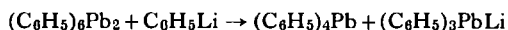
The cleavage of hexaorganodilead compounds with metals was first reported in 1939, when triphenylleadsodium was prepared by the action of

sodium in liquid ammonia on hexaphenyldilead (and other hexaorgano-dileads) (296, 297, 312). Further investigation (300, 301) showed that lithium, potassium, rubidium, calcium, strontium, or barium reacted with hexaphenyldilead in a similar fashion. A study of the relative yields of  $R_3PbM$  compounds produced from hexaphenyldilead and various metals,



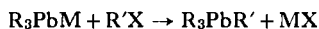
has also been carried out (364). The yields of  $R_3PbM$  compounds in this latter study were estimated by derivatization with an alkyl halide (preferably benzyl chloride) followed by determination of the amount of  $R_3PbR'$  formed.

The cleavage of hexacyclohexyldilead by continued shaking with sodium in ether has been described (324, 365). Formation of  $(C_6H_5)_3PbLi$  has also been reported (366) from the reaction of hexaphenyldilead with phenyllithium.



A more recent report (150) describes the cleavage of hexaphenyldilead by lithium in tetrahydrofuran. This latter procedure eliminates the use of liquid ammonia, and affords excellent yields of the  $R_3PbLi$  derivative.

The metal cleavage reaction is an important synthetic approach to the reactive  $R_3PbM$  derivatives. In turn, these latter compounds are useful intermediates for the preparation of unsymmetrical tetraorganolead compounds.



## VI

### GENERAL TRENDS

#### A. Physical Properties

In general, the thermal stabilities of analogous catenated compounds of the Group IVB elements decrease from silicon to lead. For example, hexaphenyldisilane melts without decomposition at 368°–370° C; the corresponding digermene shows the same behavior, melting at 352°–354° C. Hexaphenylditin, on the other hand, melts at 237° C and begins to decompose at 250° C (189), while the dilead decomposes at 155°–160° C and



deposits lead at 225° C (296, 307). Thermally induced disproportionation of ditin and dilead compounds commonly occurs at relatively low temperatures, while disilanes and digermanes are much more stable. It should be pointed out immediately that the rather sparse data in the literature make correlations difficult and possibly misleading. Comparisons of the decomposition temperatures of solid products are often the only parallelisms available, but factors such as crystal lattice energies are obviously involved in determining the decomposition points, and these factors cannot be adequately taken into account.

The stability of inorganic polysilanes has been reported to decrease with increasing chain length (3); however, a similar behavior with organic Group IVB derivatives has not become apparent except, perhaps, with polylead compounds. Decaphenylcyclopentatin decomposes at 270° C (236), which may be compared to 250° C for hexaphenylditin (189). Likewise, chain-branching may even increase stability, for tetrakis(triphenylstannyl)tin is reported to begin decomposition at 280° C (without melting) (189). Another possible indication of this effect is the fact that tetrakis(triphenylplumbyl)lead may be prepared (15, 321), and is relatively stable, while no other lead compounds containing more than two contiguous lead atoms are known.

Pyrolysis experiments on silicon and germanium hydrides have led to interesting conclusions about bond stabilities. Thermal decomposition of disilane (3) occurs at temperatures several hundred degrees lower than that required for thermal cracking of simple hydrocarbons (367). It seems reasonable to suppose, however, that the relative polarities of the Si—H and C—H bonds are important in this connection, and that the pyrolysis pathways will be dissimilar. Indeed, ethylene is a major product of the cracking of ethane (367), while silicon will not form stable double bonds. Decomposition of various hydrides and mixtures of hydrides, followed by vapor-phase chromatographic analysis of the products, showed that Ge—Ge bonds are more readily broken than Si—Ge bonds, while Si—Si links were not broken at all under the conditions employed (368). However, generalities as to the stabilities of M—M' bonds are not yet possible.

What appears to be anomalously low thermal stability is often observed with alkyl-substituted ditins and dileads. The case of hexamethylditin (204, 206) is noted in the section on physical properties of tin compounds. The series of relative stabilities of hexaorganodileads (296) might also be viewed critically. The relatively high stability of hexacyclohexyldilead (in compari-

son with the hexamethyl and hexaethyl derivatives) is particularly disturbing in that series. It should be noted that the cyclohexyl compound is a solid and may be purified by crystallization, while other hexaalkyldileads are liquids and notoriously difficult to purify, since they decompose on attempted distillation. The low stabilities of the alkyl derivatives may thus be due to impurities or possibly also to oxidative decomposition rather than strictly thermal disproportionation. Thus, the tempting generality that alkyl derivatives are less thermally stable than their aryl counterparts is perhaps not valid.

It does appear that substitution of strongly electron withdrawing groups tends to decrease the stability of the M—M bond. For instance, the recently prepared hexachloroditin disproportionates spontaneously below 0° C into a mixture of stannous and stannic chloride (288). This behavior is in marked contrast to that of the organic substituted ditins. Tetrabromo-1,2-diphenyldigermane also displays considerable instability relative to other organodigermanes, being unstable to heat and even being converted to tribromophenylgermane in solution (158). It is not known, however, whether the rate-determining step in these disproportionations is indeed the scission of the M—M bond, so that factors other than mere bond stability may be involved.

Spectral investigations definitely indicate changes in bond character with increasing chain lengths in the catenated compounds. The postulate of increasing *s* character in the Sn—Sn bond with increasing chain length has been made on the basis of nuclear magnetic resonance studies (211). Also, the presence of *dπ*–*dπ* conjugation in Si—Si bonds has been suggested by chemical (81, 134) and spectral (108, 121) data. Particularly significant is the rather regular increase in wavelength and extinction coefficient for ultraviolet absorptions of polysilanes with increasing length of the silicon chain (118, 119). There are reports that all of the Group IVB elements exhibit strong ultraviolet absorptions which are characteristic of the M—M bonds (92, 119, 262a, 341a). Further investigations to clarify the nature of the excitations observed are being made.

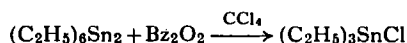
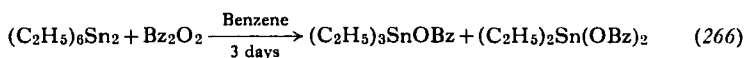
Of fundamental significance in comparing the properties of the catenated Group IVB elements is the energy of the M—M bond. There is not general agreement in the literature concerning the values of these bond energies. For instance, the Ge—Ge bond energy has been calculated to be 62 kcal mole<sup>-1</sup> from the heat of combustion of hexaethyldigermane (184), while measurement of the heat of explosive decomposition of digermane in the

presence of stibine led to a value of  $37.9 \text{ kcal mole}^{-1}$  (122). In the latter study, however, disilane and ethane were treated in the same manner with the following results: C—C,  $78.8 \text{ kcal mole}^{-1}$ ; Si—Si,  $46.4 \text{ kcal mole}^{-1}$ . The latter values, being measured by the same procedure, are likely to give a more reliable comparison of the relative bond energies. However, recent reports show that the energy of the Si—Si bonds in both inorganic (123, 124) and organic (125) derivatives is comparable to that of the C—C bond. A value of  $50 \text{ kcal mole}^{-1}$  has been calculated for the Sn—Sn bond from heat of reaction of hexaethylditin with benzoyl peroxide (253), but no information is available for the Pb—Pb bond. In spite of some anomalous observations, it does appear that bond energies decrease rather steadily from silicon to lead.

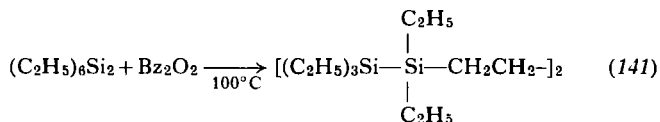
### B. Chemical Properties

The conclusions about bond energies are borne out to some extent by the relative reactivities of the M—M bonds, although some caution must be used in interpreting reactivity data. One might conclude that the carbon-carbon bond is more susceptible to homolytic cleavage than even the tin-tin or lead-lead bonds if only the  $(\text{C}_6\text{H}_5)_6\text{M}_2$  derivatives are considered. It is well known that hexaphenylethane spontaneously dissociates into triphenylmethyl radicals, while evidence for the dissociation of hexaphenyldilead under comparably mild conditions has been sought in vain (338, 347, 350). Even hexamesityldilead exists solely as the  $\text{R}_6\text{Pb}_2$  species in dilute benzene solutions (346). Thus, the generalization which might be drawn from this data is certainly invalid, because hexaphenylethane is anomalous. Steric crowding of phenyl groups is drastically different around the carbon-carbon bond from that in the dilead. It is also probable that resonance stabilization will be much more important for  $(\text{C}_6\text{H}_5)_3\text{C}\cdot$  than for  $(\text{C}_6\text{H}_5)_3\text{Pb}\cdot$ . The generalization which should be made is precisely the opposite one, namely, that homolytic cleavage becomes easier on going from carbon to lead.

Oxidative cleavage of the silicon-silicon bond is much less easily accomplished than for the tin-tin and lead-lead bonds. As a specific example, hexaethylditin and -dilead react with benzoyl peroxide with cleavage of the M—M bond.



In contrast, the reaction with hexaethyldisilane is believed to lead to a product in which the silicon-silicon bond has not been broken.



Electrophilic cleavages of the tin-tin and lead-lead bonds are in general rather easy to accomplish. Reaction of both hexaalkyl and hexaarylditins and dileads with iodine proceeds rapidly and apparently quantitatively. In contrast, hexaalkyldisilanes may be cleaved by halogens, but the aryl derivatives are rather resistant. Hexaphenyldigermane is not affected by iodine in refluxing chloroform (185), although it is cleaved by bromine in refluxing carbon tetrachloride (152). The cleavage of the digermane by bromine is reported to be slower than the corresponding reaction with hexaphenylditin, although no actual rate data were quoted (152). It appears that polysilanes and polygermanes are of rather similar reactivity toward electrophilic reagents, no major differences having become apparent in the literature. This might be expected from considerations of size and electronegativity of the two elements, although the Ge—Ge bond energy appears to be less than that for the Si—Si bond. There does appear to be a major break between germanium and tin, the polytins being considerably more reactive. The dileads continue the trend and are the most reactive.

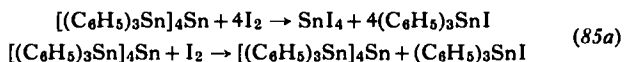
In the area of nucleophilic cleavage of the M—M bond there is less definitive data. Certainly, the silicon-silicon bond is cleaved more readily than the carbon-carbon bond, but digermanes, ditins, and dileads are cleaved under conditions similar to those required for disilanes.

The hexaaryldisilanes, germanes, tins, and leads are all readily cleaved by lithium in tetrahydrofuran. Hexaalkyldisilanes (4, 5) and digermanes (149) are resistant to cleavage by lithium, but hexa-*n*-butylditin reacts rather readily (220), and the same would presumably be the case for hexaalkyldileads. Some support for this latter suggestion is found in the facile cleavage of hexacyclohexyldilead by sodium in diethyl ether (324).

All of the M—M bonds may be cleaved by organolithium reagents, but differences in reactivity are not at present apparent. In view of the results cited above for lithium and the hexaalkyl derivatives, a similar trend may be expected with these latter compounds and organometallic reagents.

### C. Catenation

From the information that can be gathered in the literature, it undoubtedly is true that the tendency toward catenation decreases going down Group IVB. A variety of measures of M—M bond stability indicate this fact. However, there appears to be no theoretical limit to the possible length of a polysilane, polygermane, or polystannane chain. Indeed, dimethylsilyl polymers have been prepared, and in one case an average degree of polymerization of 55 units is reported (102). Exactly how long the chains in these polymers may be, or the degree of chain-branching is at present not known. Compounds which had been reported in the earlier literature to be divalent tin species,  $R_2Sn$ , have been shown to be polymeric (11). The degree of polymerization in these compounds is not usually high, as there appears to be considerable tendency to terminate through cyclization to form ring structures. The largest of these cycles thus far characterized is octadecaethylcyclononatin (188). There is at present only one polylead derivative known with a chain length of greater than two lead atoms. That compound is tetrakis(triphenylplumbyl)lead (15, 321), one of a series of related tetrakis compounds containing the Group IVB elements which appear to have rather unusual stability. A fairly large number of these compounds is now known, containing Si, Ge, Sn, or Pb either as the central atom or in a lateral position (200a). Some of the chemistry of  $[(CH_3)_3Si]_4Si$  (22, 46) and  $[(C_6H_5)_3Sn]_4Sn$  (85a, 189, 190) has been investigated, and attempts to cleave only one M—M bond in the compounds have had little success. It appears that the primary cleavage products are much more reactive than the tetrakis compounds.



The most probable reason for this behavior is steric hindrance to attack in the tetrakis structure.

The limit to chain length that does exist for Group IVB elements other than carbon is a practical one, namely, restricted synthetic methods. The great variety of condensation reactions in carbon chemistry involving double bonds does not exist for Si, Ge, Sn, and Pb. An excellent example of the laborious routes which must often be employed is afforded by the studies of Kumada on the preparation of permethylated polysilanes (1, 18). He has succeeded in preparing the compounds up to a chain length of 10 Si atoms by condensing methylchlorosilanes with sodium, replacing a terminal methyl



imaginative investigations will reveal other properties of practical importance.

#### ACKNOWLEDGMENTS

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# Cyclobutadiene-Metal Complexes

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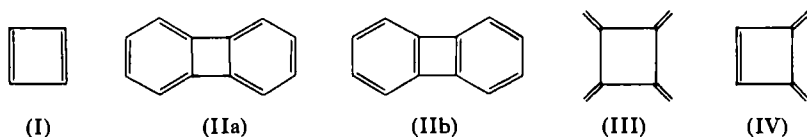
## I

### INTRODUCTION AND HISTORICAL BACKGROUND

The recognition of the aromatic properties of benzene led workers to investigate similar hydrocarbons with the general formula  $C_nH_n$ . Since the monocyclic systems where  $n$  is an odd integer cannot have a closed cyclic system

of double bonds conjugated all round the ring except when  $C_nH_n$  is an ion or radical, interest first centered on  $C_8H_8$ , cyclooctatetraene, and  $C_4H_4$ , cyclobutadiene. Cyclooctatetraene was synthesized by a classical route by Willstätter *et al.* (95) and was later obtained by Reppe *et al.* (84) from a nickel cyanide catalyzed tetramerization of acetylene.

The first attempt at the synthesis of cyclobutadiene (I), also by Willstätter (94) in 1905 was not successful. Since then numerous workers have attempted to prepare cyclobutadiene and its derivatives. Although no stable simple derivatives have been obtained, evidence has accumulated which appears to point to the intermediacy of cyclobutadienes in some reactions (7, 8, 92a).

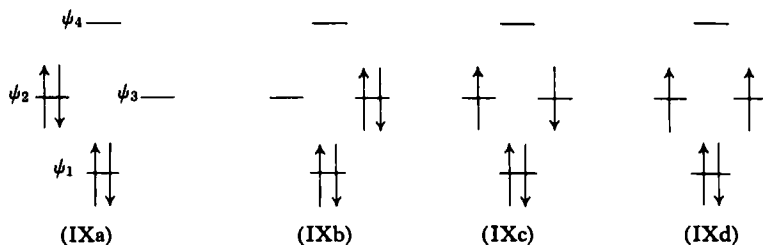


The only apparent exceptions are the annelated polybenzocyclobutadienes. The first one, biphenylene (II), was prepared by Lothrop in 1941 (61), and many derivatives are now known (7, 8). It has, however, become clear from this work that even those are best regarded not as derivatives of cyclobutadiene (I), but of either tetramethylenecyclobutane (III) or 3,4-dimethylenecyclobutene (IV). Both of these parent molecules have been synthesized (11, 48) and found to be relatively stable (at low temperatures and in the absence of oxygen) in contrast to cyclobutadiene. Thus an X-ray structure determination of biphenylene by Mak and Trotter (73) suggests that  $\pi$ -electron localization exists to give an alternation of bond orders best expressed by formula (IIa), that is, the Kekulé form (IIa) is more important than (IIb). This effect shows up very clearly in the relative stabilities of the dinaphthocyclobutadienes where (V) is found to be considerably more stable than (VI) (20, 33). This can be understood in terms of naphthalenes favoring electron localization in the 1,2- rather than in the 2,3-bonds, which facilitates a tetramethylenecyclobutane Kekulé structure for (V). Such a structure cannot, however, be written for (VI) without involving other unfavorable structures such as *o*-quinonoid ones. Similarly, while (VII) has been prepared by Cava and his co-workers, (VIII) could not be isolated (19). A dimethylenecyclobutene structure for (VII) is supported by NMR evidence. No dimethylenecyclobutene Kekulé structure can be written for (VIII) without involving *o*-quinonoid structures. Coulson *et al.*

The main reason for the instability of square cyclobutadiene can be understood by considering the  $\pi$ -electron distribution. By combination of the four  $2p_x$  carbon atomic orbitals, four molecular orbitals are formed, one of low energy,  $\psi_1$ , which is bonding, one of high energy,  $\psi_4$ , which is antibonding, and two of intermediate energy,  $\psi_2$  and  $\psi_3$ , which are degenerate and non-bonding. Since we have four electrons to place in these orbitals, four different electron configurations are possible: three singlets (IXa), (IXb), and (IXc), and one triplet (IXd).

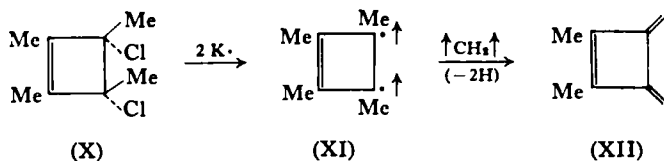
To a first approximation the energies of these states are the same and it can be shown that the total energy (4 $\beta$ ) is the same as that of two isolated double bonds. In other words, the delocalization energy is zero. Using Hund's rules, it would now appear that the diradical triplet state (IXd)

should have the lowest energy since electronic repulsions are least here. One other possibility also exists, that the molecule can distort from a square to a



rectangular shape with unconjugated single and double bonds. In this case, the most stable state would be a singlet. Calculations have been carried out (49, 58, 88) on the relative energies of the distorted and square shapes; the results are not conclusive, but suggest that a great deal of stabilization will not be gained by such a deformation; however, see Dewar and Gleicher (34a). Lipscomb (59) has even suggested that  $C_4H_4$  may be more stable with a tetrahedral arrangement of the four carbons, by analogy with  $B_4Cl_4$ .

In support of the prediction that cyclobutadiene is likely to have a triplet ground state, Skell and Petersen (87) have recently examined the reactions of the species obtained by gas-phase reaction of 3,4-dichlorotetramethylcyclobutene (X) with potassium. They found that the dehalogenated species (XI) behaved as a molecule in the triplet state would be expected to, particularly in its reaction with triplet methylene to give 1,2-dimethyl-3,4-dimethylenecyclobutene (XII) and hence proposed this as the first direct evidence for the existence of a cyclobutadiene as an intermediate.



Some chemical evidence favoring a triplet state for tetraphenylcyclobutadiene has also been presented (40).

In 1956, Longuet-Higgins and Orgel (60) pointed out that since square cyclobutadiene, according to molecular orbital theory, has two unpaired electrons in a doubly degenerate orbital, both could be used to form  $\pi$  bonds to a transition metal. They regarded the situation as analogous to that of a

cyclopentadienyl radical  $C_5H_5\cdot$  which has one unpaired electron available for  $\pi$ -bond formation to a transition metal.

The main differences between a cyclobutadiene-metal and a cyclopentadienyl-metal bond were considered to be (i) that cyclobutadiene has four  $\pi$  electrons, whereas the  $C_5H_5\cdot$  radical has five; (ii) the former will form two  $\pi$  bonds to the metal, whereas the latter will only form one; and (iii) cyclobutadiene-metal complexes will only have one  $\delta$  bond by back-coordination from the metal to the ring. They therefore predicted that cyclobutadiene-metal complexes might well be even more stable than cyclopentadienyl-metal complexes. The possibility that a cyclobutadiene might bond to the metal as two acetylenes they rejected, since the electronic states of acetylenes are unfavorable for strong bond formation to transition metals. Longuet-Higgins and Orgel also proposed that both 16- and 18-electron complexes would be formed, the former in complexes derived from positive ions (such as  $C_4H_4AuCl_2^+$ ) and the latter in formally zero-valent complexes such as  $C_4H_4Ni(CO)_2$ . They also proposed that cyclobutadiene complexes might be formed in the reactions of acetylenes with palladium(II) or auric(III) chlorides and that a cyclobutadienenickel complex might be an intermediate in the Reppe synthesis of cyclooctatetraene (see Section VIII).

The main predictions of this remarkable paper were rapidly fulfilled by the preparation of tetramethylcyclobutadienenickel chloride (XIV) by Criegee and Schroeder (32) and very shortly afterwards of tetraphenylcyclobutadieneiron tricarbonyl (XIII) by Hübel and his co-workers (52, 53).

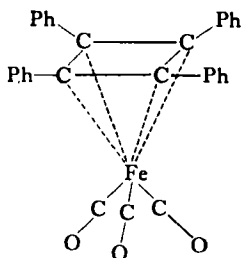
## II

### STRUCTURES OF THE CYCLOBUTADIENE-METAL COMPLEXES

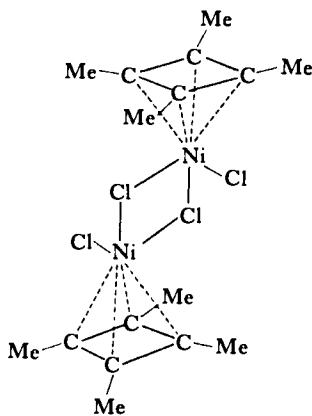
Accurate X-ray structure determinations have so far been carried out on two complexes, tetramethylcyclobutadienenickel chloride (XIV) (36) and tetraphenylcyclobutadieneiron tricarbonyl (XIII) (35). A remarkable feature is the similarity of the two structures with respect to the central metal atom.

The iron complex has a square-planar cyclobutadiene ring with C—C distances averaging 1.46 Å and internal bond angles  $90^\circ \pm 1^\circ$ . The substituent phenyl groups are bent back out of the plane of the cyclobutadiene ring away from the iron by an average of  $11^\circ$  and are all twisted about the

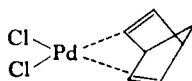
cyclobutadiene-phenyl bond in the same direction. The iron-cyclobutadiene carbon distances are all the same (2.06 Å) and are the same as the iron-carbon distances in ferrocene (37); similarly, the cyclobutadiene C—C distances are close to those in ferrocene (1.40 Å).



(XIII)



(XIV)



(XV)

The crystals of the nickel complex (XIV) used for the structure determination contained benzene of crystallization. These benzene molecules do not take part in the bonding and are found between two units. Contrary to expectations (60) the units consist of dimers of tetramethylcyclobutadiene-nickel chloride linked by two chlorine bridges, giving each nickel the krypton closed-shell configuration. Due to the disorder in the position of the benzene solvate molecules in the crystal, the results here are not quite as accurate as those obtained for the iron complex (XIII) but again the cyclobutadiene ring carbon-carbon distances average 1.43 Å and the nickel-carbon distances, 2.02 Å, are very nearly all equal. The internal angles in the cyclobutadiene ring are  $91^\circ \pm 2^\circ$  and the methyl groups are folded back away from the nickel atom and are 0.12–0.18 Å away from the plane of the cyclobutadiene ring.

In both molecules each central metal atom has the cyclobutadiene ring on one side and three other ligands (CO or Cl) on the other. These three ligands in both cases lie at an angle of about  $120^\circ$  to a line joining the mid-point of the cyclobutadiene ring and the metal atom.

The reason for the dimeric nature of the tetramethylcyclobutadienenickel chloride complex in the solid is somewhat puzzling. A similar result is to be expected for the tetraphenylcyclobutadienenickel and -palladium halides [e.g., (XXXIII) and (XXXVII)] structure determinations of which have not yet been carried out. The related tetrakis(*p*-chlorophenyl)cyclobutadienepalladium bromide (XXXVI;  $R = p\text{-ClC}_6\text{H}_4$ ,  $X = \text{Br}$ ) has been shown to be dimeric in chloroform solution (70), but the insolubility of the other tetraphenylcyclobutadienepalladium and -nickel halides in noncomplexing solvents precludes molecular weight determinations. It appears probable, however, that all these complexes are dimeric with a formally five-coordinate metal atom if the cyclobutadiene is considered to be a bidentate ligand. This is in contrast to such apparently similar complexes as norbornadienepalladium chloride (XV) which is monomeric and where the palladium(II) has an almost square-planar arrangement of the ligands (6). It can be argued, on the basis of the angle which the diene subtends at the metal, that it would be better to consider a cyclobutadiene as a large monodentate rather than a bidentate ligand. This angle is  $45^\circ$  for (XIII) and (XIV), but is  $71^\circ$  for the norbornadiene complex (XV), and may be the reason why the nickel-(II) and palladium(II) go to higher coordination numbers in their cyclobutadiene complexes. In this case the complexes (XIII) and (XIV) can best be regarded as distorted tetrahedral.

### III

#### BONDING IN CYCLOBUTADIENE-METAL COMPLEXES

Modified molecular orbital descriptions of the metal-ring bonding in these complexes have been given (23, 16). Coates' treatment (23) of the bonding in tetramethylcyclobutadienenickel chloride dimer is used here.

The three  $\pi$  orbitals of cyclobutadiene,  $\psi_1$ ,  $\psi_2$  and  $\psi_3$  (Section I) which are involved in the bonding are represented in Fig. 1. The highest energy orbital,  $\psi_4$ , has a node between each carbon atom and can combine with the nickel  $d_{x^2-y^2}$  orbital. However, the high energy of  $\psi_4$  probably makes the bonding molecular orbital mainly  $d_{x^2-y^2}$  and the antibonding molecular orbital mainly  $\psi_4$ . Hence this is not an important bonding combination.

Bonding between the lowest energy orbital  $\psi_1$  and the metal will be possible using metal orbitals of the correct symmetry, that is, those which



are independent of rotation about the  $z$  axis,  $3d_{xz}$ ,  $4s$ , and  $4p_z$ . Two hybrid orbitals can be constructed by combination of the  $d_{xz}$  and the  $s$  orbitals,  $ha_g = (d_{xz} + s)$  concentrated in the  $xy$  plane, and  $ka_g = (d_{xz} - s)$  directed along the  $z$  axis. In combination with  $p_z$  the latter forms two strongly directional orbitals,  $(ka_g + p_z)$  and  $(ka_g - p_z)$ . The  $(ka_g + p_z)$  orbital points away from the cyclobutadiene ring and is available for bonding to the other ligands, while  $(ka_g - p_z)$  can combine with  $\psi_1$  to form a bonding orbital  $(\psi_1 + ka_g - p_z)$ . The main bonding, as in the metal cyclopentadienyls, will probably be between  $\psi_2$  and  $(d_{xz} - p_x)$ , and  $\psi_3$  and  $(d_{yz} - p_y)$ . The remaining combinations  $(d_{xz} + p_x)$ ,  $(d_{yz} + p_y)$ , and  $(ka_g + p_z)$  are available for bonding to the three chlorine atoms on the other side of the nickel. In addition, two orbitals,

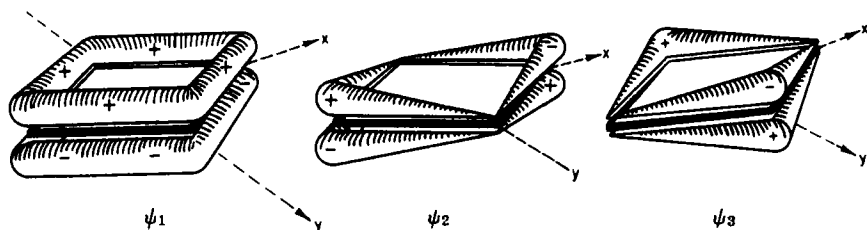


FIG. 1. Pictorial representation of the three lowest energy molecular orbitals of cyclobutadiene [after Coates (23)].

$d_{xy}$  and  $ha_g$ , which are concentrated in the  $xy$  plane and point away from the ligands are suited as nonbonding orbitals. The distribution of 18 electrons in nine orbitals will then be

$$(\psi_1 + ka_g - p_z)^2 (\psi_2 + d_{xz} - p_x)^2 (\psi_3 + d_{yz} - p_y)^2 (\psi_4 + d_{x^2-y^2})^2 (ha_g)^2 (d_{xy})^2 (ka_g + p_z)^2 \\ (d_{xz} + p_x)^2 (d_{yz} + p_y)^2.$$

This treatment can, with suitable modifications where necessary, explain the bonding in many of the presently known cyclobutadiene-metal complexes, especially those with three ligands in addition to the cyclobutadiene ring.

#### IV

#### PREPARATION OF CYCLOBUTADIENE-METAL COMPLEXES

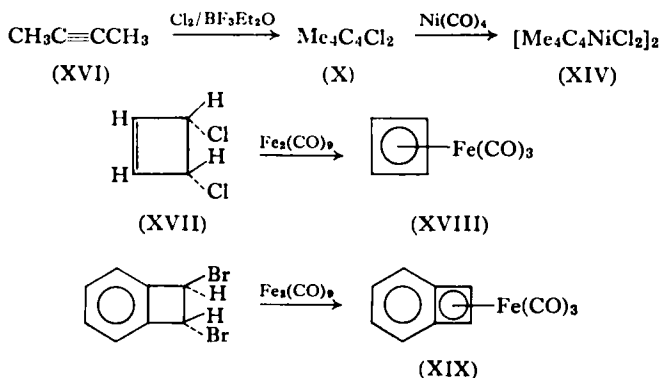
The routes by which the first complexes, (XIII) and (XIV), were prepared, from an acetylene and from a 3,4-dihalocyclobutene, respectively, represent

the most important direct methods of synthesis. The disadvantages lie in the unpredictability of the first type of reaction (only diphenylacetylene and some substituted diphenylacetylenes have as yet definitely been shown to undergo these reactions) and in the difficulty in preparing the dihalocyclobutenes. For synthesis of cyclobutadiene complexes of different metals the ligand-transfer reactions hold most promise (Section IV, F). All the major methods by which cyclobutadiene-metal complexes have been prepared are described below. In addition, reactions of cyclobutadiene complexes where the metal-cyclobutadiene bond is not broken (e.g., replacement of CO by another ligand) are discussed in Section VI, G.

### A. From 3,4-Dihalocyclobutenes

The potentially most straightforward synthesis is by dehalogenation of a 3,4-dihalocyclobutene by a metal or metal(0) complex where the resultant cyclobutadiene can then immediately form a complex with the metal. The limitations of this method are the difficulty of preparing most 3,4-dihalocyclobutenes and that the dehalogenating agent must be chosen with considerable care since in some cases dimers of the cyclobutadiene rather than metal complexes thereof are formed. Three complexes have, however, been made by this method.

Criegee and Schroeder (32), adapting a previously described synthesis, were able to prepare 3,4-dichloro-1,2,3,4-tetramethylcyclobutene (X)



directly from 2-butyne (XVI). Reaction of (X) with nickel carbonyl under mild conditions in a variety of solvents gave tetramethylcyclobutadiene-nickel chloride (XIV).

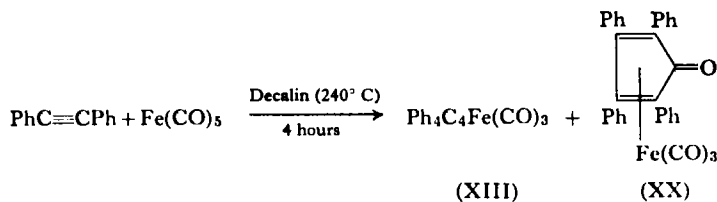
Pettit *et al.* (38) have recently described a modification using *cis*-3,4-dichlorocyclobutene (XVII) and  $\text{Fe}_2(\text{CO})_9$  to prepare the parent cyclobutadieneiron tricarbonyl (XVIII). Benzocyclobutadieneiron tricarbonyl (XIX) was similarly prepared. (See also the Appendix.)

Criegee has also prepared tetramethylcyclobutadieneiron iodide from 3,4-diiodotetramethylcyclobutene and Raney nickel (28). On the other hand, *cis,cis*-1,4-diiodotetraphenylbutadiene did not undergo this reaction either with  $\text{Ni}(\text{CO})_4$  or Raney nickel (10).

The course of the reaction, and the nature of the product formed in these reactions are not readily predictable. It appears, however, that there is a high tendency for cyclobutadiene complexes with a  $d^8$  central metal ion [ $\text{Fe}(0)$ ,  $\text{Co}(\text{I})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Pd}(\text{II})$ ] to exist. This may serve as a useful guide to future work.

### B. From Acetylenes and Metal Carbonyls

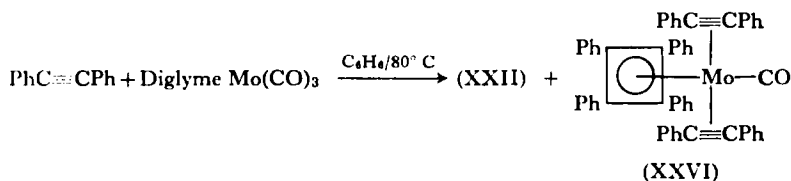
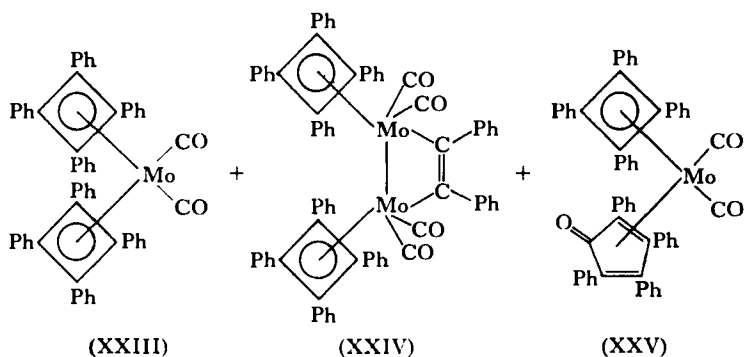
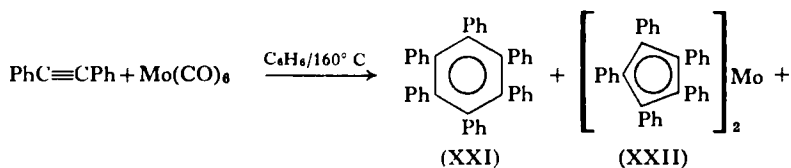
The reactions of metal carbonyls with acetylenes have been extensively studied. In general, mixtures of products are obtained including acetylenic dimers and trimers and their metal complexes and complexes in which carbon monoxide has been incorporated into the organic moiety. While these reactions are not useful synthetically due to the large number of products obtained and the difficulty in separating them, they are very interesting from a mechanistic point of view. Hübel *et al.* (51, 53) showed that one of the products from a high-temperature reaction of diphenylacetylene with iron pentacarbonyl was tetraphenylcyclobutadieneiron tricarbonyl (XIII), obtained in 16% yield together with the tetracyclone complex (XX) as major product. Interestingly enough, at lower temperatures no (XIII) was formed, but trace amounts were obtained from the reaction of diphenylacetylene with  $\text{Fe}_3(\text{CO})_{12}$  at  $90^\circ\text{C}$  (52), the main product then being the binuclear complex  $(\text{PhC}_2\text{Ph})_2\text{Fe}_2(\text{CO})_6$  (XXXIV).



Bis(*p*-chlorophenyl)acetylene undergoes a similar reaction to give tetrakis(*p*-chlorophenyl)cyclobutadieneiron tricarbonyl in 8% yield (14). Cyclo-

octatetraeneiron tricarbonyl also reacted at high temperatures with diphenylacetylene to give a 4% yield of (XIII); at lower temperatures the main product was (XXXIV) again (80).

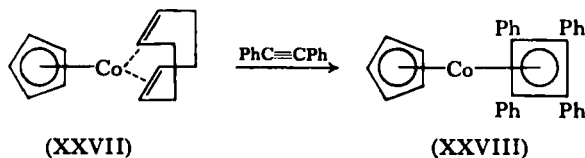
Another reaction which appears to yield tetraphenylcyclobutadiene complexes is that between molybdenum hexacarbonyl or diglymemolybdenum tricarbonyl and diphenylacetylene (54).



### C. From Acetylenes and Other Transition Metal Complexes

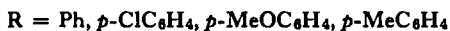
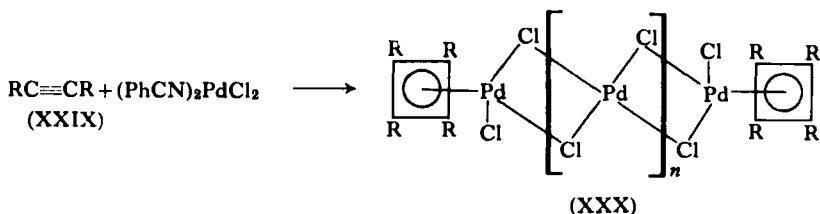
As iron forms cyclobutadiene complexes preferentially in the (0) oxidation state, the best starting materials for these complexes are Fe(0) compounds such as the carbonyls. Cobalt, however, tends to form Co(I) (also  $d^8$ ) cyclobutadiene complexes. The best known one (cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (XXVIII), has been prepared from cyclopentadienylcobalt(I) derivatives and also from cobaltocene, a cobalt(II)

complex. While cyclopentadienylcobalt dicarbonyl reacts with diphenylacetylene to form a tetracyclone complex (75), cyclopentadienylcobalt-diene complexes such as (cyclopentadienyl)(1,5-cyclooctadiene)cobalt (XXVII) react with the acetylene to give (XXVIII) in 30–50% yield (78, 79). It is obtained in similar yield from cobaltocene and diphenylacetylene (13).



The former reaction is very sensitive to conditions; thus while ( $\pi$ -cyclopentadiene)( $\pi$ -cyclopentadienyl)cobalt(I) reacted with diphenylacetylene in toluene to give (XXVIII) in 30% yield, in tetrahydrofuran the products were tetraphenylbutadiene and ( $\pi$ -cyclopentadienyl)( $\pi$ -tetraphenylbutadiene)cobalt(I) (78).

The reaction between diphenylacetylenes and palladium chloride can give a number of products and is further discussed in Sections IV, E and VI, F. Under some conditions, however, direct formation of a tetraphenylcyclobutadienepalladium chloride can occur (70).

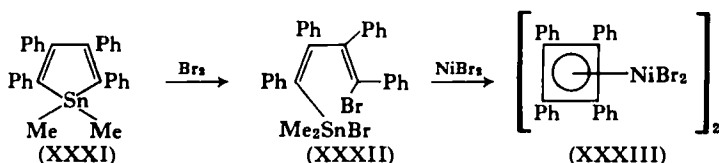


The other product is the hexaphenylbenzene [e.g., (XXI) for  $R = \text{Ph}$ ] and the relative proportions obtained depend greatly on the method of addition and solvent used (25, 41, 55, 69, 70), high dilution, and addition of the acetylene to the bis(benzonitrile)palladium chloride favoring the formation of (XXX). The catenated complex (XXX) can be converted into the normal tetraphenylcyclobutadienepalladium chloride (XXX,  $n = 0$ ) (55, 70) [Section VI, G].

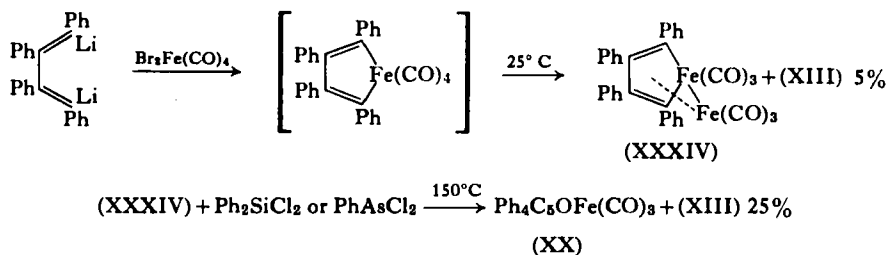
Other acetylenes also react with palladium chloride; the products obtained do not for the most part appear to be cyclobutadiene complexes.

### D. From 1-Heterocyclopentadienes

Freedman (40) used a novel method to prepare tetraphenylcyclobutadiene-nickel bromide (XXXIII) from 1,1-dimethyl-2,3,4,5-tetraphenylstannole (XXXI) which was obtained from 1,4-dilithiotetraphenylbutadiene and dimethyltin dichloride. The stannole (XXXI) is cleaved by one mole of bromine to the butadiene (XXXII), which on refluxing with nickel bromide in triglyme gave the cyclobutadiene (XXXIII) in high yield.



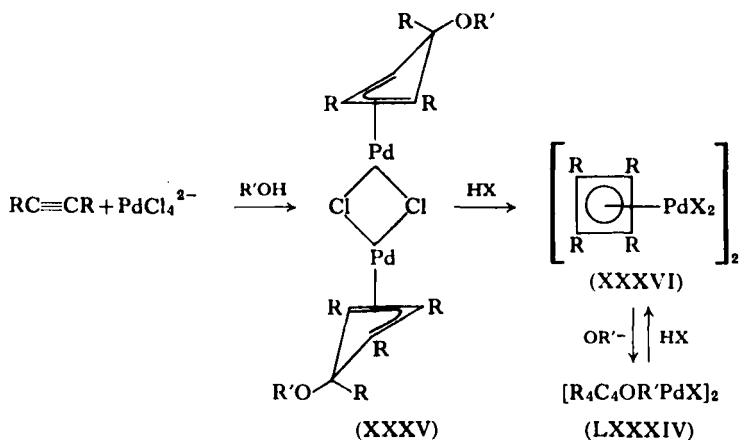
Somewhat analogous methods have been used (50, 51) to prepare tetraphenylcyclobutadieneiron tricarbonyl (XIII).



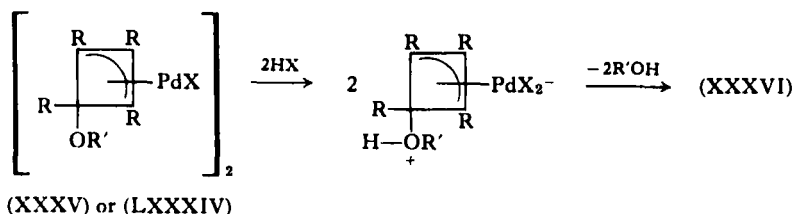
### E. From $\pi$ -Cyclobutenyl Complexes

Malatesta *et al.* (74) first studied the reaction between diphenylacetylene (XXIX; R = Ph) and palladium chloride in ethanol and suggested that the product was a  $\sigma$ - and  $\pi$ -bonded ethoxytetraphenylcyclobutenepalladium chloride dimer. Subsequent investigations (12, 25, 91) confirmed the stoichiometry of the product and an X-ray structure determination (34) has shown the complex to have a structure close to that originally suggested and to be an ethoxytetraphenylcyclobutenylpalladium chloride dimer, with the ethoxy group *endo* to (on the same side as) the metal (XXXV; R = Ph, R' = Et). A number of similar complexes with R = Ph, R' = Me and R = *p*-ClC<sub>6</sub>H<sub>4</sub>, R' = Et and also with different bridging halogens have been prepared (70, 91). All these complexes (XXXV) react with hydrogen halides to give tetraphenylcyclobutadienepalladium halides (XXXVI). Improved

preparations of (XXXV) and (XXXVI) have been published (68); the reaction in the absence of ethanol has already been mentioned [Section IV, C].



The cyclobutadienepalladium complexes (XXXVI) react with alcohols, usually in the presence of weak bases, to give cyclobutenylpalladium complexes (LXXXIV) isomeric with (XXXV) (see Section VI, F); these reactions are reversed on treatment of (LXXXIV) with hydrogen halides and constitute another preparation of the cyclobutadienepalladium complexes. A related reaction on  $(\pi\text{-cyclopentadienyl})(\pi\text{-alkoxytetraphenylcyclobutenyl})$ palladium and -nickel complexes (XLIV) (64, 65) is also discussed in Section VI, F. The mechanism of this reaction is not established, but the initial step is probably protonation of the ether.

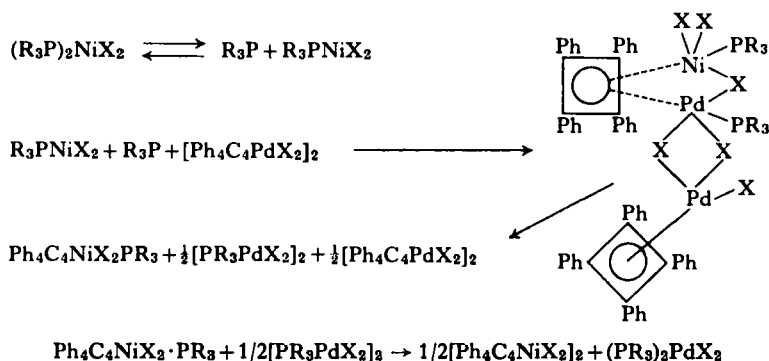


#### F. From Other Cyclobutadiene-Metal Complexes by Ligand-Exchange and Ligand-Transfer Reactions

Except for the dehalogenation reactions described by Pettit *et al.* (38) all the previous methods of synthesis involve acetylenes at some stage. As these

reactions are highly specific both with regard to the metal and the acetylene, these syntheses are really unique and not easily extended to other cyclobutadienes and other metals. The former problem has not yet been overcome but the synthesis, especially of tetraphenylcyclobutadiene complexes of various metals, has been simplified by ligand-exchange and ligand-transfer reactions.

As described in Section VI, D, tetraphenylcyclobutadienepalladium halides react with *tert*-phosphines to liberate the organic ligand which is obtained as the dimer, octaphenylcyclooctatetraene (XLIII) (72). The phosphines in bis(*tert*-phosphine)nickel halides are quite labile and on reaction of these compounds with tetraphenylcyclobutadienepalladium halides exchange of the ligands occurs (69). A suggested mechanism is as shown.



This method is, however, only of very limited applicability. The ligand-transfer reactions in which tetraphenylcyclobutadienepalladium halides [usually the bromide (XXXVII)], react with metal carbonyls or other transition metal compounds in low oxidation states are more useful. In general, the cyclobutadiene group is transferred, frequently in high yield, from the palladium onto the other metal, but there are exceptions (Section VI, G). For example, in the reaction of  $\pi$ -cyclopentadienyliron dicarbonyl bromide with (XXXIII), (XXXVII), or (XXXIX) the cyclopentadienyl and not the tetraphenylcyclobutadiene group is transferred (64, 65). Figure 2 summarizes the main reactions which have been carried out (62, 63, 66, 67, 71). The tetrakis(*p*-chlorophenyl)cyclobutadiene group has also been transferred from palladium onto iron (70) and one ligand transfer in the opposite direction has also been accomplished (69).



These reactions are usually heterogeneous, hence no meaningful data on their mechanisms have yet been obtained. It appears, however, that the reactions illustrated in Fig. 2 which occur under reducing conditions and where the metal carbonyls function as dehalogenating agents, probably go by paths as outlined in Fig. 3. In this scheme two main steps are envisioned,

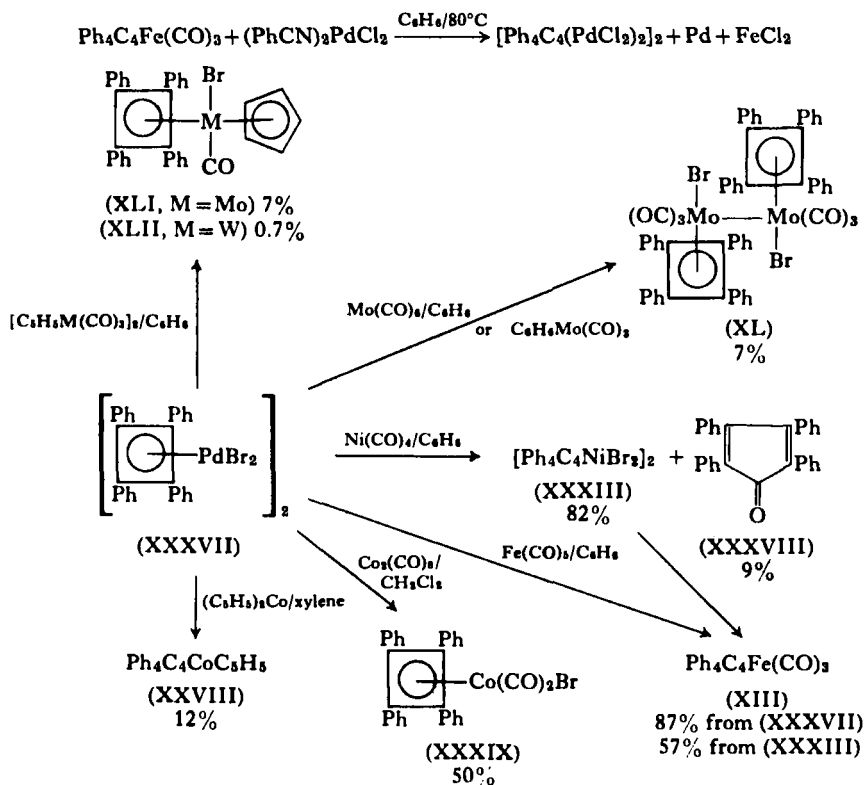


FIG. 2. Synthesis of cyclobutadiene-metal complexes by ligand-transfer reactions.

the first being complex formation between the carbonyl and the cyclobutadienepalladium halide, possibly with loss of CO, and the second, in which the cyclobutadiene is transferred from the palladium to the other metal, with loss of CO and some reorganization. Since products are obtained corresponding to the transfer of one, two, or no halogen, a single reaction scheme is not possible. Modifications must also be made in the reactions of substituted metal carbonyls with (XXXVII). In none of these reactions is

the cyclobutadiene group assumed to become free but rather a transfer inside a complex is envisioned (see also Section VIII). However, the formation of organic side products (especially when the yield of complex is low) such as octaphenylcyclooctatetraene (XLIII) and tetracyclone (XXXVIII) suggests that while the first step leading to the breakup of the palladium complex is always efficient, the second step is sometimes very difficult. This leads to the formation of organic products rather than a complex.

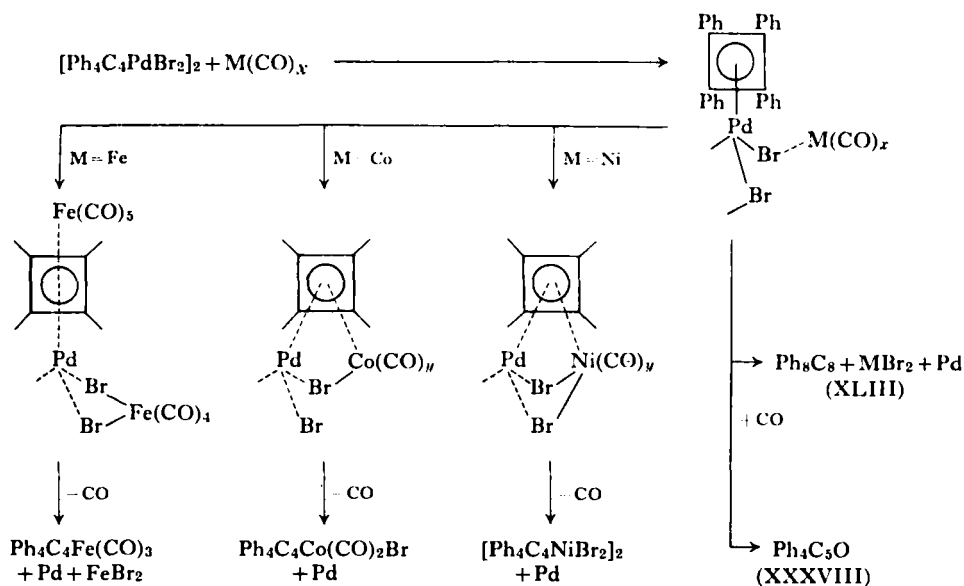


FIG. 3. Proposed mechanism for the ligand-transfer reactions.

These reactions are extremely sensitive to conditions, e.g., temperature, solvent, etc. The best one is the reaction of the palladium complex (XXXVII) with iron pentacarbonyl to give (XIII). At  $80^\circ\text{C}$  the yield ranges from 87% in benzene, cyclohexane, or 1,2-dichloroethane, to 17% in tetrahydrofuran-diglyme and is zero in carbon tetrachloride (71). The reaction of (XXXVII) with molybdenum hexacarbonyl only occurs in aromatic hydrocarbon solvents and since the complex (XL) is obtained in the same yield starting from either molybdenum hexacarbonyl or benzenemolybdenum tricarbonyl, it is reasonable to assume the latter to be an intermediate in this reaction.

## V

PROPERTIES OF CYCLOBUTADIENE-METAL  
COMPLEXES

## A. General

All the cyclobutadiene-metal complexes, the structures of which are reasonably well established at the time of writing (August, 1965), are listed in Table I together with some of their key properties (see also Appendix). It will be seen that all these complexes obey the Effective Atomic Number formalism if the cyclobutadiene is assumed to donate four electrons. With two exceptions, tetraphenylcyclobutadienecobalt dicarbonyl bromide (XXXIX) and its triphenylphosphine derivative, all the complexes are diamagnetic. The cobalt complex (XXXIX), however, shows anomalous magnetic behavior and exhibits a paramagnetism corresponding to the presence of two unpaired electrons at 25° C (63). This is unusual, since (XXXIX) is a Co(I) complex which should be diamagnetic in a strong crystal field. In contrast, the tetraphenylcyclobutadienemolybdenum tricarbonyl halides are dimeric and diamagnetic. To account for these properties a structure with a metal-metal bond (XL) has been proposed (67). No evidence has yet been found for the existence of square-planar cyclobutadiene-metal complexes where the metal has an effective atomic number two less than the next inert gas, which were predicted by Longuet-Higgins and Orgel (60). One of the molybdenum complexes recently prepared by Hübel and Merenyi (54), formulated as (XXVI), may, however, be of this type.

In addition to those listed in Table I, a number of other complexes thought to contain cyclobutadiene ligands but where the evidence is not unambiguous, are dealt with in Section VII. One of the most difficult problems in this field is in fact to decide whether or not a given complex is a cyclobutadiene derivative. This problem is particularly acute in the reaction products of acetylenes with transition metal compounds where large numbers of complexes involving extremely unusual bonding are often obtained. In some cases infrared or NMR spectra can be useful (Section V, D); when this is not so, the problem can usually be solved only by an X-ray structure determination.

Chemical degradations of the complexes have been used to assign structures but the results are often difficult to interpret since no definitive test

TABLE I  
CYCLOBUTADIENE-METAL COMPLEXES

Ligand	Formula	Formula number in text <sup>a</sup>	Properties	Method of preparation <sup>a</sup>	References
Cyclobutadiene <sup>b</sup>	C <sub>4</sub> H <sub>4</sub> Fe(CO) <sub>3</sub>	(XVIII)	M.p. 26° C; b.p. 68°–70° C/3 mm; ν <sub>CO</sub> ; 1985, 2055 cm <sup>-1</sup>	IV, A	38
1,2,3,4-Tetra- methylcyclo- butadiene	[Me <sub>4</sub> C <sub>4</sub> NiCl <sub>2</sub> ] <sub>2</sub>	(XIV)	—	IV, A	32
	Me <sub>4</sub> C <sub>4</sub> NiCl <sub>2</sub> PPh <sub>3</sub> <sup>c</sup>	—	—	VI, G	28
	Me <sub>4</sub> C <sub>4</sub> NiCl <sub>2</sub> ·C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> ·2H <sub>2</sub> O <sup>c</sup>	—	—	VI, G	29
	[Me <sub>4</sub> C <sub>4</sub> NiI <sub>2</sub> ] <sub>2</sub> <sup>c</sup>	—	—	IV, A	28
1,2,3,4-Tetra- phenylcyclo- butadiene	Ph <sub>4</sub> C <sub>4</sub> Fe(CO) <sub>3</sub>	(XIII)	M.p. 234° C (35, 80)	IV, A	51, 52, 53, 80
				IV, D	50, 51
				IV, F	66, 71
	Ph <sub>4</sub> C <sub>4</sub> Co(CO) <sub>2</sub> Br	(XXXIX)	M.p. 255°–262° C <sup>d</sup> ; ν <sub>CO</sub> : 2037, 2072 cm <sup>-1</sup>	IV, F	63
	Ph <sub>4</sub> C <sub>4</sub> Co(CO)(Ph <sub>3</sub> P)Br	—	M.p. 225°–230° C <sup>d</sup> ; ν <sub>CO</sub> ; 1988 cm <sup>-1</sup>	VI, G	63
	Ph <sub>4</sub> C <sub>4</sub> CoC <sub>5</sub> H <sub>5</sub>	(XXVIII)	M.p. 256° C (78, 79); 264° C (13)	IV, C	13, 78, 79
				IV, F	64, 65, 66
	[Ph <sub>4</sub> C <sub>4</sub> CoC <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> Br <sup>-</sup>	(LXXXVIII)	M.p. 170°–180° C <sup>d</sup>	VI, G	63
	[Ph <sub>4</sub> C <sub>4</sub> CoCH <sub>3</sub> C <sub>6</sub> H <sub>5</sub> ] <sup>+</sup> Br <sup>-</sup>	(LXXXVIII)	M.p. 170°–172° C <sup>d</sup>	VI, G	63
	[Ph <sub>4</sub> C <sub>4</sub> Co-1,3,5-(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>3</sub> ] <sup>+</sup> Br <sup>-</sup>	(LXXXVIII)	M.p. 160° C <sup>d</sup>	VI, G	63
	[Ph <sub>4</sub> C <sub>4</sub> NiBr <sub>2</sub> ] <sub>2</sub> <sup>c</sup>	(XXXIII)	316° C <sup>d</sup>	IV, D	40
				IV, F	66, 69, 71

TABLE I—*continued*

Ligand	Formula	Formula number in text <sup>a</sup>	Properties	Method of preparation <sup>a</sup>	References
1,2,3,4-Tetra-phenylcyclobutadiene	$\text{Ph}_4\text{C}_4\text{NiBr}_2\text{PPh}_3^c$	—	—	VI, G	41
	$[\text{Ph}_4\text{C}_4\text{NiC}_5\text{H}_5]^+\text{FeBr}_4^-$	(LXXXVII)	—	VI, G	64, 65
	$[\text{Ph}_4\text{C}_4\text{NiC}_5\text{H}_5]^+\text{Br}^-$	(XLIV)	M.p. 193° C <sup>d</sup>	VI, G	64, 65
	$[\text{Ph}_4\text{C}_4\text{Mo}(\text{CO})_3\text{Br}]_2$	(XL)	M.p. 280° C <sup>d</sup> ; $\nu_{\text{CO}}$ ; 1976, 2026 $\text{cm}^{-1}$	IV, F	67
	$[\text{Ph}_4\text{C}_4\text{Mo}(\text{CO})_3\text{I}]_2$	—	M.p. 290° C <sup>d</sup> ; $\nu_{\text{CO}}$ ; 1974, 2021 $\text{cm}^{-1}$	IV, F	67
	$(\text{Ph}_4\text{C}_4)_2\text{Mo}(\text{CO})_2$	(XXIII)	M.p. 255°–260° C; $\nu_{\text{CO}}$ 1961, 2004 $\text{cm}^{-1}$	IV, B	54
	$[\text{Ph}_4\text{C}_4\text{Mo}(\text{CO})_2]_2\text{PhC}_2\text{Ph}$	(XXIV)	M.p. 200°–205° C; $\nu_{\text{CO}}$ 1927, 1949, 1988 $\text{cm}^{-1}$	IV, B	54
	$(\text{Ph}_4\text{C}_4)(\text{Ph}_4\text{C}_5\text{O})\text{Mo}(\text{CO})_2$	(XXV)	M.p. 240°–243° C; $\nu_{\text{CO}}$ 1618 (ketone), 1953, 2012 $\text{cm}^{-1}$	IV, B	54
	$(\text{Ph}_4\text{C}_4)\text{Mo}(\text{PhC}_2\text{Ph})_2(\text{CO})$	(XXVI)	M.p. 200°–202° C; $\nu_{\text{CO}}$ 2024 $\text{cm}^{-1}$	IV, B	54
	$(\text{Ph}_4\text{C}_4)(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})\text{Cl}$	(XLI)	M.p. 261–266° C <sup>d</sup> ; $\nu_{\text{CO}}$ 1973 $\text{cm}^{-1}$	IV, F	62
	$(\text{Ph}_4\text{C}_4)(\text{C}_5\text{H}_5)\text{Mo}(\text{CO})\text{Br}$	(XLI)	M.p. 248–250° C <sup>d</sup> ; $\nu_{\text{CO}}$ 1998 $\text{cm}^{-1}$	IV, F	62
	$[\text{Ph}_4\text{C}_4\text{PdCl}_2]_2^c$	(LIV)	M.p. 282°–285° C (25); 297°–298° C <sup>d</sup> (68); 311° C <sup>d</sup> (91)	IV, E IV, F	12, 25, 68, 91 69
	$[\text{Ph}_4\text{C}_4(\text{PdCl}_2)_{1.5}]_2^c$	(XXX)	M.p. 305°–307° C <sup>d</sup> (55)	IV, C	25, 55
	$[\text{Ph}_4\text{C}_4(\text{PdCl}_2)_{2.5}]_2^c$	(XXX)	—	IV, C	70

	$[\text{Ph}_4\text{C}_4(\text{PdCl}_2)_3]_2^c$	(XXX)	—	IV, C	70
	$[\text{Ph}_4\text{C}_4\text{PdBr}_2]_2^c$	(XXXVII)	M.p. 347°–348° C <sup>d</sup> (68); 320° C <sup>d</sup> (91)	IV, E VI, G	65, 68, 69, 91 91
	$[\text{Ph}_4\text{C}_4\text{PdI}_2]_2^c$	—	M.p. 287°–290° C <sup>d</sup> (68); 236° C <sup>d</sup> (91)	IV, E VI, G	68, 91 91
	$[\text{Ph}_4\text{C}_4\text{PdC}_5\text{H}_5]^+ \text{FeBr}_4^-$	(LXXXVII)	—	VI, G	64, 65
	$[\text{Ph}_4\text{C}_4\text{PdC}_5\text{H}_5]^+ \text{Br}^-$	(XLIV)	M.p. 187° C <sup>d</sup>	VI, G	64, 65
	$(\text{Ph}_4\text{C}_4)(\text{C}_5\text{H}_5)\text{W}(\text{CO})\text{Br}$	(XLII)	M.p. 227°–228° C <sup>d</sup> ; $\nu_{\text{CO}}$ 1958 $\text{cm}^{-1}$	IV, F	62
Tetrakis( <i>p</i> -chloro-phenyl)cyclobutadiene	$[(p\text{-ClC}_6\text{H}_4\text{C})_4\text{PdBr}_2]_2$	(XXXVI)	300° <sup>d</sup>	IV, E; VI, G	70
	$[(p\text{-ClC}_6\text{H}_4\text{C})_4(\text{PdCl}_2)_2]_2^c$	(XXX)	M.p. 244°–248° <sup>d</sup>	IV, C	70
	$[(p\text{-ClC}_6\text{H}_4\text{C})_4(\text{PdCl}_2)_3]_2^c$	(XXX)	M.p. 232°–234° <sup>d</sup>	IV, C	70
	$(p\text{-ClC}_6\text{H}_4\text{C})_4\text{Fe}(\text{CO})_3$	—	M.p. 242° (70); $\nu_{\text{CO}}$ 1978, 2025 $\text{cm}^{-1}$ (70)	IV, F; IV, B	14, 70
Tetrakis( <i>p</i> -methoxyphenyl)-cyclobutadiene	$[(p\text{-MeOC}_6\text{H}_4\text{C})_4\text{PdCl}_2]_2^c$	(XXX)	—	VI, G	69
	$[(p\text{-MeOC}_6\text{H}_4\text{C})_4(\text{PdCl}_2)_{1.5}]_2^c$	(XXX)	—	IV, C	69
	$[(p\text{-MeOC}_6\text{H}_4\text{C})_4(\text{PdCl}_2)_3]_2^c$	(XXX)	—	IV, C	69
Benzocyclobutadiene	$\text{C}_8\text{H}_6\text{Fe}(\text{CO})_3$	(XIX)	M.p. 25° C; b.p. 73°–78° C/0.1 mm; $\nu_{\text{CO}}$ 1978, 2047 $\text{cm}^{-1}$	IV, A	38
	$\text{C}_8\text{H}_6\text{Fe}(\text{PPh}_3)(\text{CO})_2$	—	—	VI, G	38

<sup>a</sup> Refers to sections in which preparations are given in the text.

<sup>b</sup> Some monosubstituted cyclobutadiene-iron tricarbonyls and related complexes are also mentioned in the Appendix.

<sup>c</sup> Molecular size unknown; formulated by analogy to similar complexes.

<sup>d</sup> Decomposition; these values are not reliable as melting and decomposition points vary with rate of heating and depend on whether or not air is present.

reactions for cyclobutadienes are available. A further complication is that even in reactions in which the unstable cyclobutadiene is liberated, the nature of the metal has a profound influence on the further course of the reaction (28, 38, 87). Examples of unusual products obtained in degradation reactions are widespread and particularly misleading, as evidenced by the molybdenum complexes of Hübel and Merenyi (54).

### B. Stability

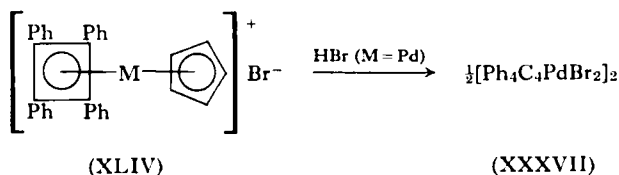
Little meaningful physical data on these complexes has appeared yet. The study of their reactivity is complicated by the effects of the substituents on the cyclobutadiene ring and the other ligands present. Until more information is available on the properties of the recently prepared unsubstituted cyclobutadieneiron tricarbonyl (XVIII) (38) and similar molecules, it is hard to be certain which properties are due to the presence of a cyclobutadiene group. Thus while cyclobutadieneiron tricarbonyl (XVIII) is easily oxidized by ferric chloride in ethanol (as are other diene-iron tricarbonyl complexes, albeit to different types of product), tetraphenylcyclobutadieneiron tricarbonyl (XIII) is very resistant to this reagent, and indeed to most others, presumably mainly due to the steric hindrance of the phenyls.

A very recent paper (39a) has now shown that cyclobutadieneiron tricarbonyl (XVIII) is an aromatic system and that it easily undergoes electrophilic substitution reactions (see Appendix).

Tetraphenylcyclobutadienepalladium and -nickel complexes and tetramethylcyclobutadienenickel chloride react readily with nucleophilic reagents to give  $\pi$ -cyclobutenyl complexes (12, 30, 31, 65, 91), a reaction reminiscent of those described by Chatt *et al.* for diene-palladium and diene-platinum halide complexes (Section VI, F). Non-halogen-containing cyclobutadiene complexes, however, appear inert under similar conditions so that this reaction is very dependent on the other ligands present. Some similarity between cyclobutadiene-metal and diene-metal complexes appears to exist but how far the parallel can be drawn remains to be seen. The reactions are fully discussed in Section VI.

All the complexes so far described possess good thermal stability (in some cases to over 300°C) and are reasonably air-stable in the solid, though in some cases air oxidation occurs quite readily in solution.

One of the predictions made by Longuet-Higgins and Orgel (60) was that a cyclobutadiene-metal bond might well be stronger than a cyclopentadienyl-metal bond. While this is very difficult to test, a suggestive



result in confirmation of this is that (cyclopentadienyl)(tetraphenylcyclobutadiene)palladium bromide (XLIV; M = Pd) is cleaved by hydrogen bromide to give tetraphenylcyclobutadienepalladium bromide (XXXVII) (65).

### C. Solubility

The solubilities of these complexes vary enormously. Some which contain either one or no halogen are freely soluble in most organic solvents, while others such as the tetraphenylcyclobutadienenickel and -palladium halides are very insoluble except in strongly coordinating solvents (such as dimethylformamide), with which they frequently react. This insolubility must be due to the presence of large dimeric units, since tetraphenylcyclobutadienepalladium chloride, for example, dissolves fairly readily in chloroform saturated with hydrogen chloride, forming presumably the  $\text{Ph}_4\text{C}_4\text{PdCl}_3^-$  ion (12). Tetrakis(*p*-chlorophenyl)cyclobutadienepalladium bromide dimer (XXXVI; R = *p*-ClC<sub>6</sub>H<sub>4</sub>, X = Br), in contrast, was sufficiently soluble in chloroform to permit a molecular weight determination (70). Tetramethylcyclobutadienenickel chloride is soluble in polar organic solvents (in which it appears to be highly associated) as well as in water (32).

In addition to the one described above, the cyclobutadienepalladium and -nickel dihalide dimers undergo other halogen-bridge splitting reactions, described in Sections VI, D and VI, G. The tetraphenylcyclobutadienepalladium chlorides also form highly insoluble complexes containing one or more bridging PdCl<sub>2</sub> groups (see Sections IV, C and VI, G).



### D. Spectra

Infrared and ultraviolet spectra of some cyclobutadiene complexes have been published (12, 13, 32, 47, 79, 91). Fritz (47)<sup>1</sup> has also attempted to correlate infrared band positions with the stretching and bending modes of the complexes. The complexity of the molecules, however, makes this very difficult; no unambiguous assignment of the ultraviolet spectral bands is yet possible either.

In the absence of other groups having characteristic bands in the 2–16  $\mu$  region, however, the infrared spectra can be very useful as diagnostic tests for the presence of cyclobutadiene ligands in complexes if appropriate spectra of complexes of known structure are available for comparison. This has been widely used in the tetraphenylcyclobutadiene complexes since all of these show strong family resemblances. However, this test is usually more suggestive than definitive since relative band intensities vary considerably from one complex to another and depend on the other ligands present. For example, Fritz (47) noted that a band at about 1380  $\text{cm}^{-1}$  was very intense in the tetraphenylcyclobutadiene nickel and -palladium halides. While this band appears in most other tetraphenylcyclobutadiene-metal complexes, it varies considerably in intensity and is weak when other  $\pi$ -bonding ligands are present as in tetraphenylcyclobutadieneiron tricarbonyl (XIII).

The proton NMR spectra of some of these complexes have been determined. The spectrum of cyclobutadieneiron tricarbonyl (XVIII) shows a singlet at 6.09 $\tau$  and that of benzocyclobutadieneiron tricarbonyl (XIX) a singlet at 5.98 $\tau$  due to the cyclobutadiene protons, as well as a multiplet due to the aromatic protons at 3.05 $\tau$  (38). The NMR spectra of monosubstituted cyclobutadieneiron tricarbonyls (see Appendix) show the equivalence of the two cyclobutadiene ring protons adjacent to the substituent. This implies that the four-membered ring must be square (39a). Tetramethylcyclobutadiene nickel chloride in water shows only a single resonance due to the 12 equivalent methyl protons (32). The spectra of the tetraphenylcyclobutadiene-metal complexes are those due to phenyl protons and are usually complex. In the (cyclopentadienyl)(tetraphenylcyclobutadiene)nickel and -palladium bromides (XLIV), however, sharp single phenyl proton resonances are obtained at 2.39 $\tau$  (65). The reason for the apparent equivalence of all the phenyl protons in (XLIV) is not clear.

<sup>1</sup> See the article by Fritz in Volume 1 of this series.

## VI

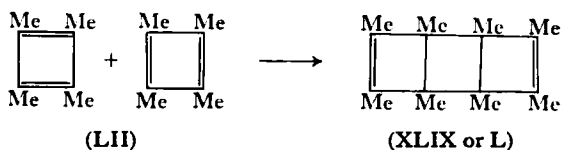
## REACTIONS OF CYCLOBUTADIENE-METAL COMPLEXES

Most of the reactions of cyclobutadiene-metal complexes so far reported were carried out with the aim of confirming the structure of the complex. As mentioned in Section V, A, however, evidence for the structure from chemical degradation is not always very convincing.

## A. Thermal Decomposition

Criegee and his co-workers (28, 29, 32) were the first to study the thermal decomposition of a cyclobutadiene complex, tetramethylcyclobutadiene-nickel chloride (XIV). The most important reactions and products obtained are summarized in Fig. 4.

Except for tetramethylbutadiene (XLVIII) and 3-methylene-1,2,4-trimethylcyclobutene (LI) all the decomposition products are dimers of tetramethylcyclobutadiene (LII). (LI) can also be derived from (LII) by a 1,3-hydrogen shift; it is an interesting commentary on the instability of the cyclobutadiene (LII) that as unstable a molecule as (LI) is formed preferentially. The butadiene (XLVIII) can also be thought of as arising from (LI) which then abstracts two hydrogens from the solvent or elsewhere. Since an inseparable mixture of (XLV) and (XLVI) is formed on heating any of the other dimers (XLVII), (XLIX), and (L) to about 200° C, the most significant products of the thermal decomposition are (XLVII), (XLIX), and (LI). The formation of the *anti*-octamethyltricyclooctadiene (XLIX) can be thought of as arising by a Diels-Alder condensation of two tetramethylcyclobutadienes (LII); the cyclooctatetraene (XLVII) may well arise by isomerization of (XLIX) (see below).



However, there are other possible explanations of how these products arise which do not involve the intermediacy of a free cyclobutadiene. One, that these dimerization or hydrogen-transfer reactions at least commence in

a metal complex is suggested by the effect of the metal on the type of product. Thus while decomposition of the nickel complex (XIV) at 100°C yields the *anti* dimer (XLIX), dehalogenation of (X) which ought, on the "free

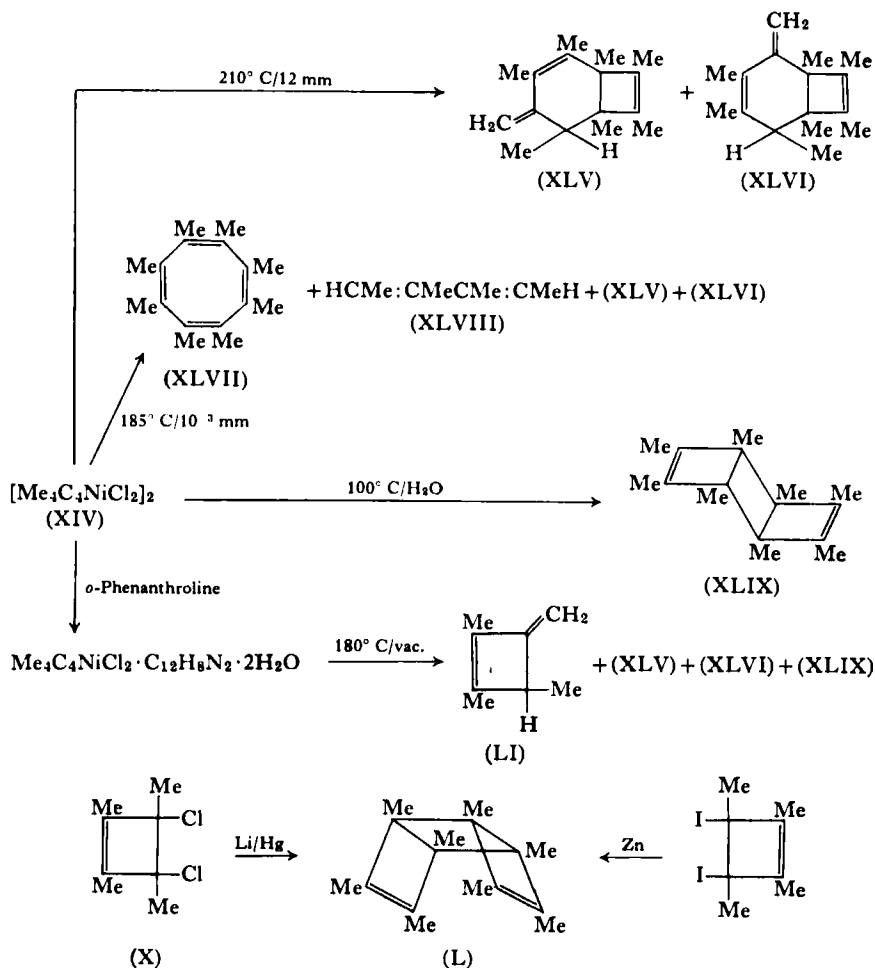
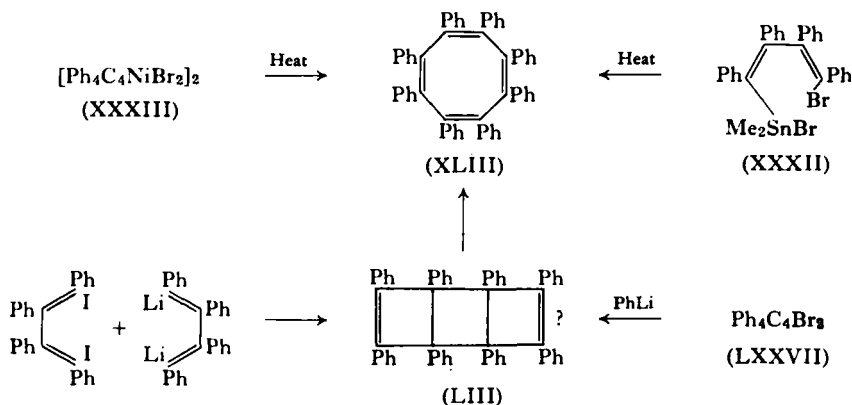


FIG. 4. Thermal decomposition of tetramethylcyclobutadienenickel chloride and related reactions.

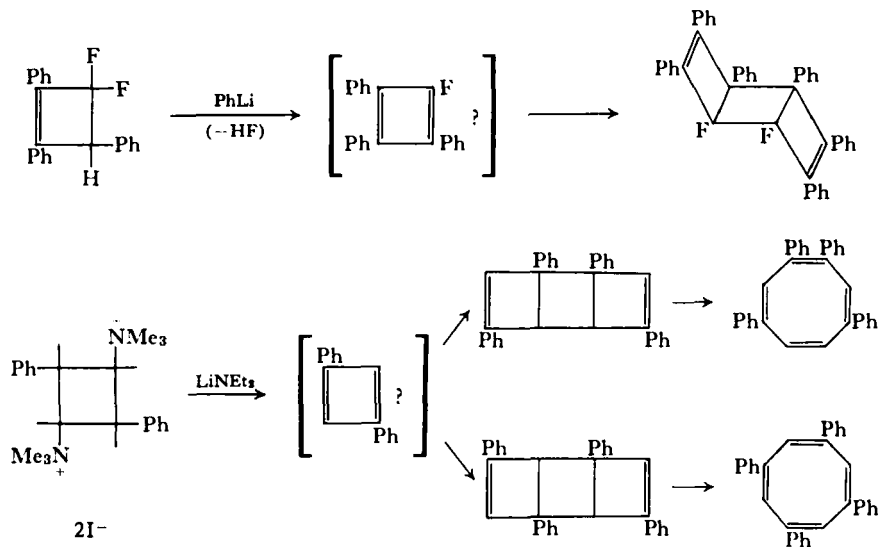
cyclobutadiene" theory, to give the same product, in fact gives the *syn* dimer (L).

Tetraphenylcyclobutadienenickel bromide (XXXIII) on pyrolysis yields nickel bromide and hydrocarbon products including octaphenylcyclo-

octatetraene<sup>2</sup> (XLIII) (40, 41). Thermal decomposition of the stannole dibromide (XXXII) also gave (XLIII) (45).



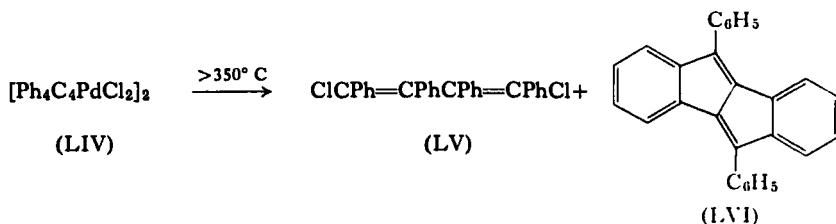
Freedman (45) was able to prepare an isomer of (XLIII), probably a tricyclooctadiene (LIII), which isomerized to (XLIII) even on standing at 25°C in the solid. This suggests that (XLIII) may also be formed from (XXXII) or (XXXIII) via (LIII). This type of dimerization product is



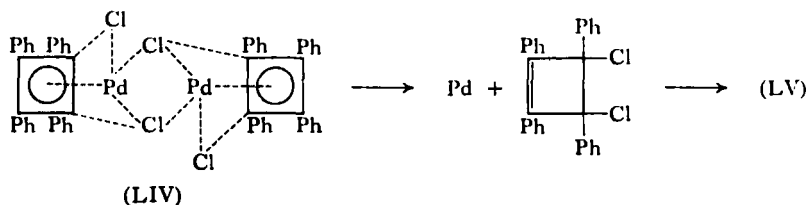
<sup>2</sup> Due to its chemical inertness and to the absence of any olefinic C=C stretching bands in the Raman spectrum, (XLIII) was first identified as octaphenylcubane. The X-ray structure determination carried out by Pawley *et al.* and by Wheatley (82) has definitely established the cyclooctatetraene structure (XLIII).

quite common in reactions where cyclobutadienes can be reasonably postulated as intermediates and several examples have recently been described (77, 93). A metal complex may play an important role here too, however.

In contrast, pyrolysis of tetraphenylcyclobutadienepalladium chloride dimer (LIV) gave palladium metal and 1,4-dichlorotetraphenylbutadiene (LV) (12).



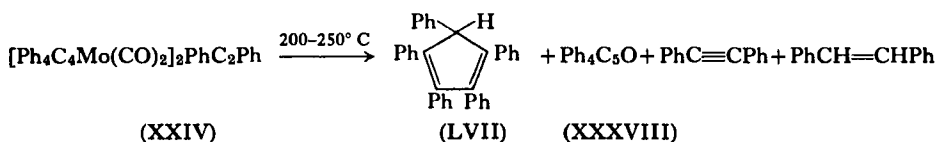
Later work showed that two isomers of (LV) were formed together with trace amounts of a diphenylindenoindene (LVI) (25). The isolation of tetraphenylfuran (LXV) from this reaction has also been reported (55); this must, however, be a by-product arising from air oxidation. The formation of the 1,4-dichlorotetraphenylbutadiene again illustrates the importance of the metal; palladium-halogen bonds are weaker than nickel-halogen bonds, hence it is reasonable to assume that on pyrolysis the whole complex breaks up to give a dichlorocyclobutene which isomerizes to (LV).



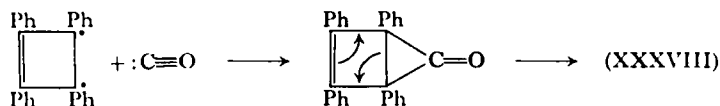
By analogy to the recent observation (43) that *cis*-tetraphenylcyclobutene (LIX) isomerizes to *cis,trans*-tetraphenylbutadiene (LX), if the dichlorotetraphenylcyclobutene formed in this reaction were *cis* then the configuration of (LV) expected would be *cis,trans*.

Hübel and Merenyi (54) have described the pyrolysis of a tetraphenylcyclobutadienemolybdenum complex to which they ascribed the structure (XXIV). The products obtained were pentaphenylcyclopentadiene (LVII), tetracyclone (XXXVIII), diphenylacetylene, and stilbene.

While (LVII) is a curious product which suggests that large reorganizations occur during pyrolysis, tetracyclone (XXXVIII) is not an unreasonable

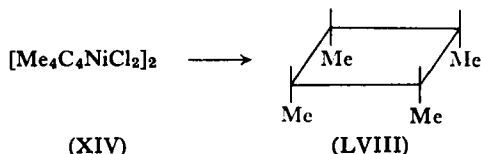


product. Vallarino and Santarella (91) have shown that at  $70^\circ\text{C}$  and under 200 atm of CO, tetraphenylcyclobutadienepalladium chloride (LIV) gave a mixture of tetracyclone (XXXVIII) and 2,3-dihydrotetracyclone (LXIII). The formation of tetracyclone during ligand-transfer reactions (Section IV, F) has also been noted (66), but the amount formed can be reduced by working at lower temperatures (71). If the free cyclobutadiene is formed under these conditions incorporation of CO can be explained as shown. Again, this is not the most probable explanation; a cyclobutadiene-metal carbonyl is a more likely intermediate with insertion of CO occurring inside the complex.



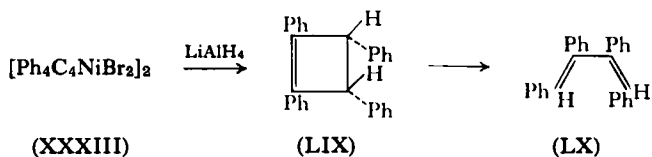
### B. Reduction

Catalytic hydrogenation or zinc-hydrochloric acid reduction of an aqueous solution of tetramethylcyclobutadienenickel chloride (XIV) gave a 90% yield of all *cis*-tetramethylcyclobutane (LVIII) (28).

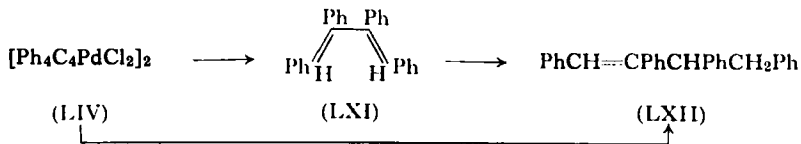


Tetraphenylcyclobutadieneiron tricarbonyl (XIII) on reduction with lithium aluminum hydride gave 1,2,3,4-tetraphenylbutadiene (52) [formerly thought to be the *trans,trans* isomer but now established as the *cis,cis* (LXI) (43)], while a sodium in liquid ammonia reduction gave 1,2,3,4-tetraphenylbutane (52).

Lithium aluminum hydride reduction of tetraphenylcyclobutadiene-nickel bromide (XXXIII) on the other hand, gave a 90% yield of *cis*-tetraphenylcyclobutene (LIX) which isomerized at 50° C to *cis,trans*-tetraphenylbutadiene (LX) (43).

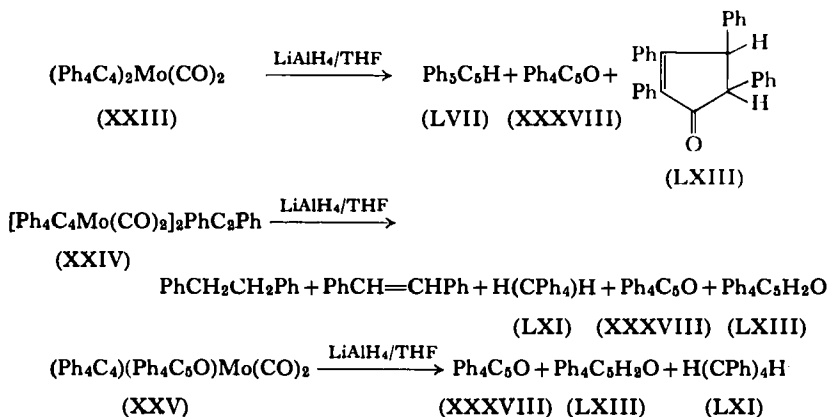


Catalytic hydrogenation of (XXXIII) at 75° C and 60 atm gave a hydrocarbon originally identified as a tetraphenylcyclobutene (40), but which has now been suggested to be tetraphenylbutene (LXII) (25). This same hydrocarbon (LXII) also appears to be obtained from catalytic hydrogenation of tetraphenylcyclobutadienepalladium chloride (LIV) under similar conditions; using milder conditions (25) or lithium aluminum hydride (25, 91), or sodium borohydride (55, 91), the product is *cis,cis*-tetraphenylbutadiene (LXI).



These reactions too may proceed via a tetraphenylcyclobutene.

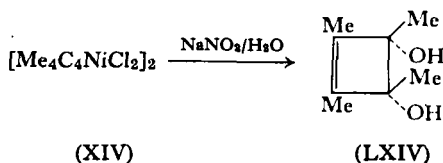
(Cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (XXVIII) appears to be inert to most reducing agents (79) but the tetraphenylcyclobutadiene-



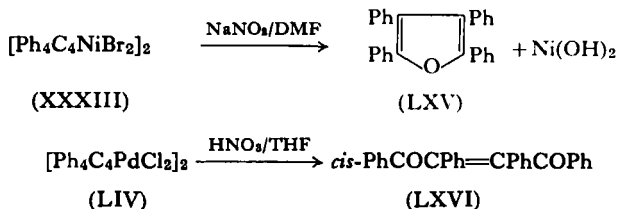
molybdenum carbonyl complexes (54) undergo some very unusual reactions on lithium aluminum hydride reduction.

### C. Oxidation

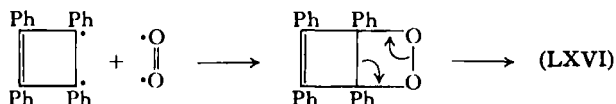
Mild oxidation of tetramethylcyclobutadienenickel chloride (XIV) with aqueous sodium nitrite gave *cis*-3,4-dihydroxy-1,2,3,4-tetramethylcyclobutene (LXIV) and was the first chemical proof of the presence of a cyclobutadiene ring in (XIV) (32).



A similar reaction on tetraphenylcyclobutadienenickel bromide (XXXIII) gave tetraphenylfuran (LXV), not the expected diol (40).



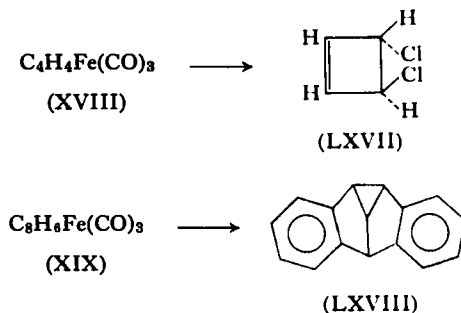
Tetraphenylcyclobutadienepalladium chloride (LIV) under more vigorous conditions gave *cis*-dibenzoylstilbene (LXVI) (55, 91). This was also obtained on treatment of (LIV) with dimethyl sulfoxide (55) and by air oxidation of a heated solution of the stannole dibromide (XXXII) (40). A mechanism for its formation from tetraphenylcyclobutadiene has been proposed (40).



Cyclobutadieneiron tricarbonyl (XVIII) on oxidation with ethanolic ferric chloride (or ceric ammonium nitrate-lithium chloride) gave *trans*-dichlorocyclobutene (LXVII) (38), and other products (92a) (see also Appendix).



Benzocyclobutadieneiron tricarbonyl (XIX) only gave polymer under these conditions, however, silver nitrate oxidation gave a dimeric hydrocarbon identified as (LXVIII). The formation of this unusual product has been suggested to proceed via a tricyclooctadiene intermediate which isomerizes to (LXVIII) (38).



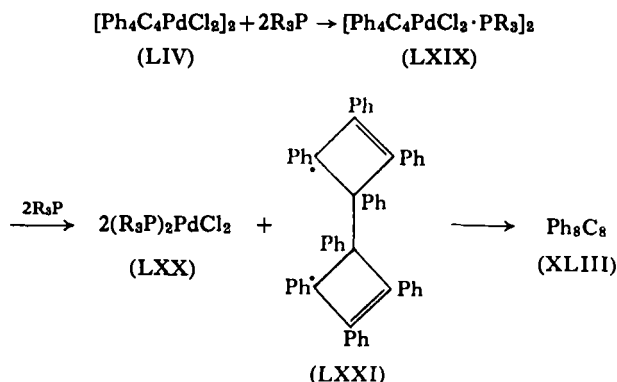
Tetraphenylcyclobutadieneiron tricarbonyl (XIII) in contrast is very inert to most oxidizing agents. However, bis(benzonitrile)palladium chloride, a mild oxidizer, causes decomposition and the formation of a tetraphenylcyclobutadienepalladium chloride (see Section IV, F) (69).

#### D. Reactions with Donor Ligands

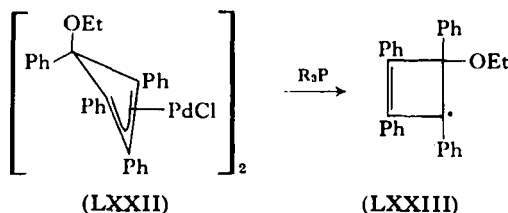
Some of the cyclobutadiene complexes [e.g., (XIII) and (XXVIII)] appear to be inert to the action of donor ligands such as phosphines, pyridine, etc. However, a number form adducts. These have not been fully described, but triphenylphosphine adducts of tetramethylcyclobutadienenickel chloride (XIV) (28) and tetraphenylcyclobutadienenickel bromide (XXXIII) (41) and an *o*-phenanthroline complex (29) of the former have been reported. Other reactions with donor molecules in which the cyclobutadiene-metal bond remains intact are mentioned in Section VI, G.

Tetraphenylcyclobutadienepalladium halides such as the chloride (LIV) react very readily with phosphines, a qualitative order of reactivity being tri-*n*-butylphosphine > 1,2-bis(diphenylphosphino)ethane > triphenylphosphine (24, 69). No adducts have been isolated, but when the reactions are run at 25°C in benzene in the absence of air, a deep green solution is obtained, which persists for some time in the case of triphenylphosphine. This solution contains a strongly paramagnetic species, the electron spin resonance spectrum of which is independent of the phosphine

(69, 72). The spectrum is very complex, but has been interpreted as due to a species such as (LXXI) (25).



An argument in favor of such a formulation is that the *endo*-ethoxytetraphenylcyclobutenylpalladium chloride dimer (LXXII) (Section IV, E) on treatment with phosphines gives a solution with a very similar electron spin resonance spectrum, thought to be due to (LXXIII) (25).

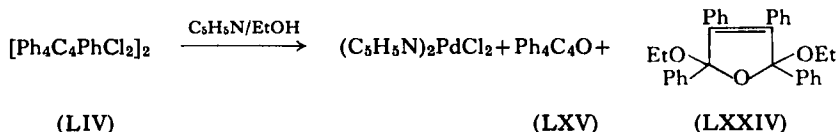


On warming the solution of (LIV) and the phosphine, the green color rapidly disappeared and the products obtained were the octaphenylcyclooctatetraene (XLIII) and the bis(*tert*-phosphine)palladium chloride (LXX). (XLIII) presumably arises from the tricyclooctadiene which is formed by coupling of the diradical (LXXI). The ligand-exchange reaction based on this has already been described in Section IV, F; none of the cyclooctatetraene (XLIII) was formed here (69).

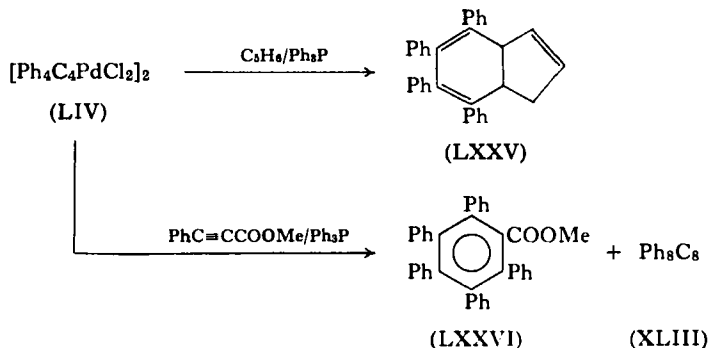
Tetrakis(*p*-chlorophenyl)- and tetrakis(*p*-methoxyphenyl)cyclobutadienepalladium halides form analogous cyclooctatetraenes on treatment with *tert*-phosphines (69, 70).

In the presence of air the yield of octaphenylcyclooctatetraene (XLIII)

is greatly reduced and the major product isolated was tetraphenylfuran (LXV) (72). Reaction of (LIV) with pyridine gave bis(pyridine)palladium chloride, tetraphenylfuran (LXV), and the diethoxydihydrotetraphenylfuran (LXXIV) (55).

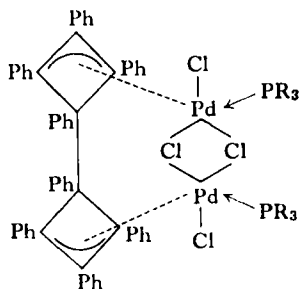


Attempts have been made to trap the free cyclobutadiene supposedly formed in the phosphine reaction with cyclopentadiene or methyl phenylpropiolate (24, 25). While the expected adducts (LXXV) and (LXXVI) were isolated, the yields, <10%, were so small as to make it doubtful that any appreciable amount of free tetraphenylcyclobutadiene, a highly reactive species, was actually present under these reaction conditions in the presence of a large excess of the diene or dienophile. The main product in the second reaction was again the cyclooctatetraene (XLIH).



The evidence for a free cyclobutadiene being formed under these reaction conditions is again ambiguous. As discussed in Section VI, A it seems much more probable that all these reactions at least begin in the metal complex. The tendency for the dimerization reaction to proceed, forming (XLIH) even in the presence of a large excess of methyl phenylpropiolate, strongly suggests that even the first step in forming the diradical (LXXI) takes place in the metal complex [e.g., (LXIX)]. If this is so, the first steps towards the formation of the adducts (LXXV) and (LXXVI) could also occur in the metal complex without primary liberation of the cyclobutadiene, and that

competition between the formation of two types of intermediate complex is the reason for obtaining two products in the latter case. However, considerable variations in mechanism can be expected, as shown by the recent claim of Pettit *et al.* to have trapped cyclobutadiene [formed by oxidation of its iron tricarbonyl complex (XVIII)] in the absence of the metal (92a).

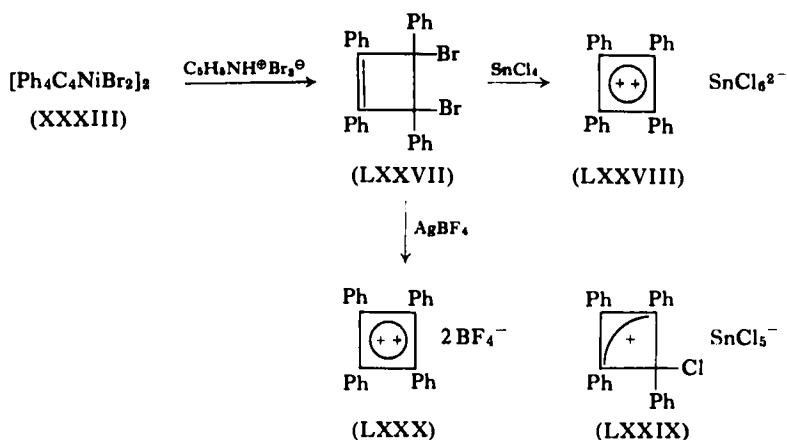


(LXIX)

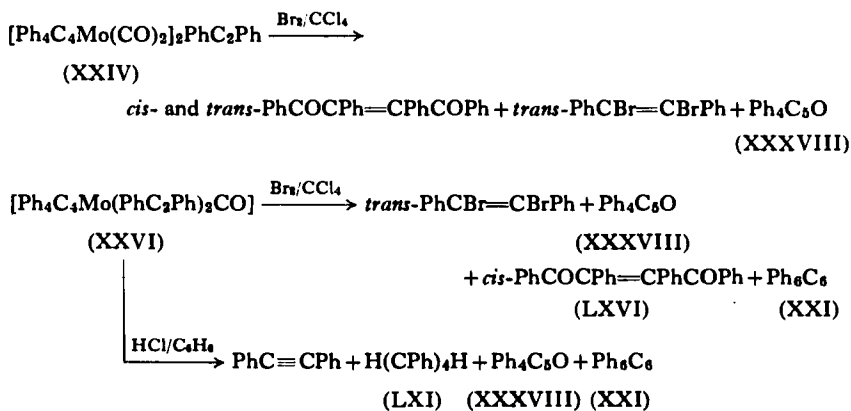
### E. Halogenation

Only two halogenation studies have been reported. Freedman *et al.* found that although treatment of tetraphenylcyclobutadienenickel bromide (XXXIII) with bromine resulted in extensive decomposition, pyridinium tribromide led to the formation of *trans*-3,4-dibromotetraphenylcyclobutane (LXXVII) in high yield (41, 42, 44). (LXXVII) underwent a series of very interesting reactions with tin and silver compounds. Treatment of (LXXVII) with stannic chloride gave an ionic compound first thought to be the hexachlorostannate (halogen exchange also occurring) of the tetraphenylcyclobutenium dication (LXXVIII) (44). However, an X-ray structure determination showed it to be the pentachlorostannate of the chlorotetraphenylcyclobutenium monocation (LXXIX) at least in the solid (17). Reaction of (LXXVII) with silver tetrafluoroborate gave two moles of silver bromide and another ionic compound, the  $F^{19}$  NMR spectrum of which shows the presence only of the  $BF_4^-$  ion. There is no evidence for a carbon-fluorine bond and hence this is postulated to be a salt of the dication (LXXX) (46).

Hübel and Merenyi (54) reported the several products listed below on bromination of two of their tetraphenylcyclobutadienemolybdenum carbonyl complexes. Hydrogen chloride also breaks up the complex (XXVI). In contrast to the products obtained from other decomposition



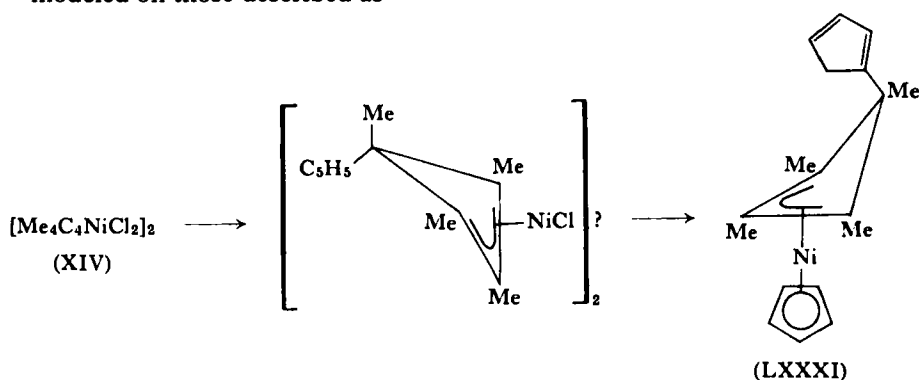
reactions of these molybdenum complexes, the formation of the products obtained here is easier to understand. The chlorine-bridge cleavage reaction in the tetraphenylcyclobutadienepalladium chlorides by hydrogen chloride has been mentioned in Section V, C.



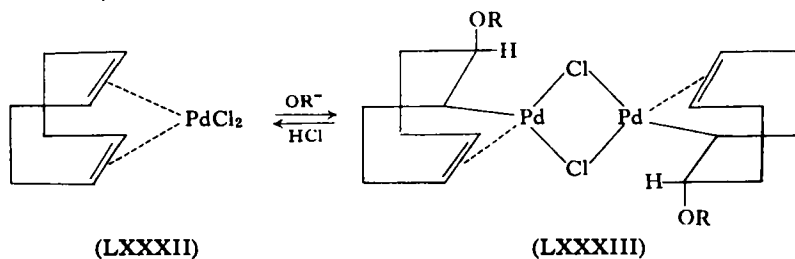
### F. Reaction with Nucleophiles

Many of the previously described reactions may well also go via an initial nucleophilic attack on the cyclobutadiene ring; however, from the products the first step is usually not obvious. In some cases, however, notably attack by alkoxide or cyclopentadienide ions, metal complexes which have been fully characterized are isolated.

Criegee and co-workers (30, 31) first reported the reaction of tetramethylcyclobutadienenickel chloride (XIV) with excess sodium cyclopentadienide. The original formulation of the product was later shown to be inconsistent with its  $H^1$  NMR spectrum (56) and a full X-ray structure determination (81) showed it to have the structure (LXXXI) with the cyclopentadienyl group *exo* to the metal. The positions of the double bonds in the cyclopentadiene ring of (LXXXI) are still in doubt and Criegee *et al.* (30) have suggested that two isomers may be present. The mechanism of the formation of (LXXXI) can most easily be understood in terms of a two-stage reaction modeled on those described as

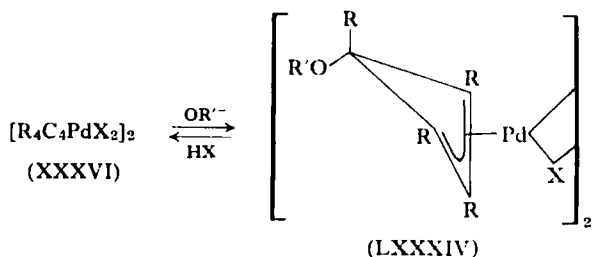


Chatt and co-workers (22) some time ago described the reactions of some unconjugated chelating diene-palladium and -platinum complexes, such as 1,5-cyclooctadienepalladium chloride (LXXXII), with alkoxide ion. In these reactions attack by  $OR^-$  occurs at a  $C=C$  to form a complex (LXXXIII) in which  $Cl^-$  has been eliminated and a  $Pd-C$   $\sigma$  bond has apparently been formed. This reaction is reversible on treatment of (LXXXIII) with  $HCl$ .



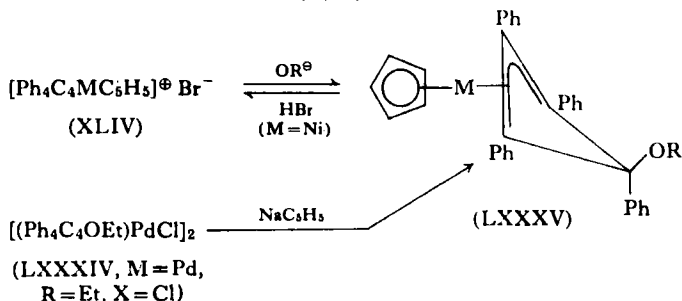
Analogous reversible reactions occur with tetraphenylcyclobutadiene-palladium halides (12, 69, 70, 91) to form cyclobutenyl complexes isomeric

with the products obtained from reactions of palladium halides with diphenylacetylenes in alcohols (Section IV, E).



Complexes (LXXXIV) have been prepared for  $R = Ph$ ,  $R' = Et$ ,  $X = Cl$ ,  $Br$ ,  $I$ , and  $SCN$  (91);  $R = Ph$ ,  $R' = Me$ ,  $X = Cl$  (91);  $R = Ph$ ,  $R' = H$ ,  $X = Cl$  (55, 91);  $R = Ph$ ,  $R' = iso-Pr$ ,  $X = Cl$  (91);  $R = p-ClC_6H_4$ ,  $R' = Et$ ,  $X = Cl$  (70); but not for  $R = p-MeOC_6H_4$ ,  $X = Cl$  (69). An X-ray structure determination of (LXXXIV,  $R = Ph$ ,  $R' = Et$ ,  $X = Cl$ ) has been carried out by Dahl and Oberhansli (81), who showed it to have the structure shown with the ethoxy group *exo* to the metal. This suggests that nucleophilic attack on (XXXVI) occurs from the side opposite to the metal. In contrast, the other isomer (XXXV) (Section IV, E) which has the ethoxy group *endo* to the metal cannot be formed from a cyclobutadiene by reaction with alkoxide but must arise by incorporation of the alkoxy group in the initial reaction of the acetylene with the palladium chloride (12). The reactions of both types of complexes have been extensively studied (12, 25, 70, 91).

This reaction has also been carried out on the (cyclopentadienyl)(tetraphenylcyclobutadiene)nickel and palladium bromides (XLIV,  $M = Ni$ ,  $Pd$ ) to give the (cyclopentadienyl)(1-*exo*-alkoxy-1,2,3,4-tetraphenylcyclobutenyl) complexes of palladium (LXXXV;  $M = Pd$ ,  $R = H$ ,  $Me$ ,  $Et$ ) and nickel (LXXXV;  $M = Ni$ ,  $R = Me$ ) (65).



The nickel complex (LXXXV;  $M = \text{Ni}$ ,  $R = \text{Me}$ ) on treatment with hydrogen bromide gave back (XLIV;  $M = \text{Ni}$ ) whereas the palladium complexes (LXXXV;  $M = \text{Pd}$ ) gave tetraphenylcyclobutadienepalladium bromide (XXXVII). (LXXXV;  $M = \text{Pd}$ ,  $R = \text{Et}$ ) was also synthesized from the chloride complex (LXXXIV;  $M = \text{Pd}$ ,  $R = \text{C}_6\text{H}_5$ ,  $R' = \text{Et}$ ) and sodium cyclopentadienide, thus confirming the structural assignments of (LXXXV).

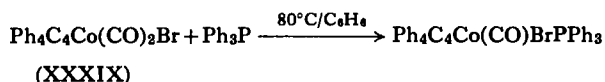
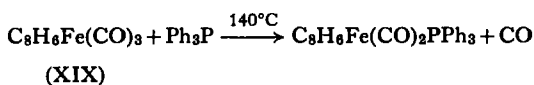
Extended reaction of tetraphenylcyclobutadienepalladium chloride (LIV) with ethanol has been reported to give tetraphenylfuran (LXV) and 1,4-diethoxytetraphenylbutadiene (25). In contrast, neither the iron complex (XIII) nor the cobalt complex (XXVIII) reacted with alkoxide (71, 79).

### G. Reactions in Which the Cyclobutadiene Ring Remains Intact

As well as the reactions mentioned above in which the cyclobutadiene-metal bond is modified or destroyed, some complexes undergo reactions in which this does not occur. Examples of this type of reaction such as halogen-bridge cleavage by phosphines in the cyclobutadiene-nickel halides have already been given in Sections V, C and VI, D. Similar reactions are the halogen-exchange reactions in both the cyclobutadienenickel and -palladium halides in which  $\text{I}^-$  displaces  $\text{Br}^-$  which displaces  $\text{Cl}^-$ . Typical conditions are (i) alkali halides in acetone (91), (ii) hydrogen halides in chloroform (69), or (iii) treatment of the halides with silver salts (83).

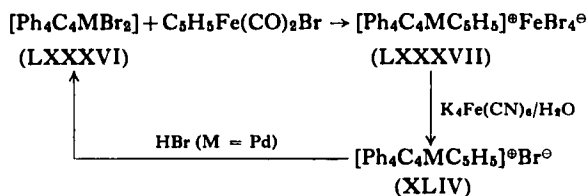
Reaction of the complexes with hydrogen bromide has also been used to break up the catenated palladium chloride complexes (XXX) (69, 70). These can also be broken up by dissolution in dimethylformamide followed by addition of hydrochloric acid, when the simple complexes (XXX;  $n = 0$ ) are obtained (55, 69).

In some cyclobutadiene metal carbonyls [e.g., (XIX) and (XXXIX)] one carbonyl can be substituted by triphenylphosphine (38, 63); tetraphenylcyclobutadieneiron tricarbonyl (XIII) however, is quite inert to triphenylphosphine.



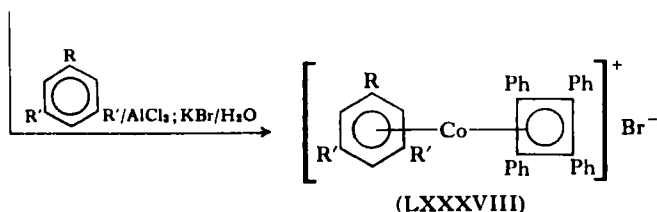
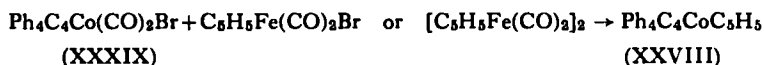


While sodium cyclopentadienide attacks tetramethylcyclobutadiene-nickel chloride both at carbon and nickel (Section VI, F), the discovery of a novel cyclopentadienylation reaction which is in effect a ligand-transfer reaction involving attack at the metal only has allowed other types of cyclobutadiene complexes to be prepared. Thus on reaction of tetraphenylcyclobutadienenickel and -palladium bromides (LXXXVI) with cyclopentadienyliron dicarbonyl bromide, the paramagnetic (cyclopentadienyl)(tetraphenylcyclobutadiene)nickel and palladium tetrabromoferrates (LXXXVII; M = Ni, Pd) are obtained (64, 65).



These are converted to the diamagnetic bromides (XLIV) on treatment with potassium ferrocyanide. The palladium complex, (XLIV; M = Pd) gave tetraphenylcyclobutadienepalladium bromide (LXXXVI; M = Pd) on reaction with hydrogen bromide. The further reactions of (XLIV) have been discussed in Section VI, F.

Tetraphenylcyclobutadienecobalt dicarbonyl bromide (XXXIX) undergoes a number of reactions in which the cyclobutadiene-cobalt bond remains intact. Thus with cyclopentadienyliron dicarbonyl bromide (or the dimer) ligand transfer again occurred to give (cyclopentadienyl)(tetraphenylcyclobutadiene)cobalt (XXVIII) (64, 65).



By analogy with other carbonyl halides, (XXXIX) reacts under Friedel-Crafts conditions with aromatic hydrocarbons (benzene, toluene, mesitylene,

etc.) to give sandwich  $\pi$  complexes such as (benzene)(tetraphenylcyclobutadiene)cobalt bromide (LXXXVIII;  $R = R' = H$ ) as well as (LXXXVIII;  $R = CH_3$ ,  $R' = H$ ;  $R = R' = CH_3$ ). In contrast to (XXXIX) and its triphenylphosphine derivative these are all diamagnetic (63).

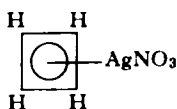
Cyclobutadieneiron tricarbonyl (XVIII) has also been shown to undergo electrophilic substitution reactions characteristic of aromatic systems to give monosubstituted cyclobutadieneiron tricarbonyl complexes (CII) (39a) (see Appendix).

## VII

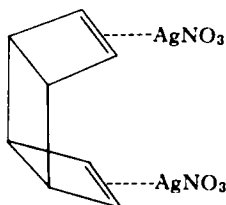
### OTHER COMPLEXES WHICH MAY CONTAIN CYCLOBUTADIENE AS A LIGAND

As a result of the difficulty of deciding on the structure of a given complex in the absence of an X-ray analysis (Section V, A), a number of complexes have been claimed to possess cyclobutadiene groups as ligands, frequently on apparently excellent grounds.

The best known of these complexes was "cyclobutadiene silver nitrate" prepared by Nenitzescu *et al.* (5). It was assigned structure (LXXXIX) on the basis of its method of preparation and some incorrect proton NMR data (4). A careful repetition of this work (3), however, showed the complex to be the di(silver nitrate) complex of *syn*-tricyclooctadiene (XC). In solution this complex isomerized to a cyclooctatetraene-silver nitrate complex which gave the originally observed (4) single proton resonance.



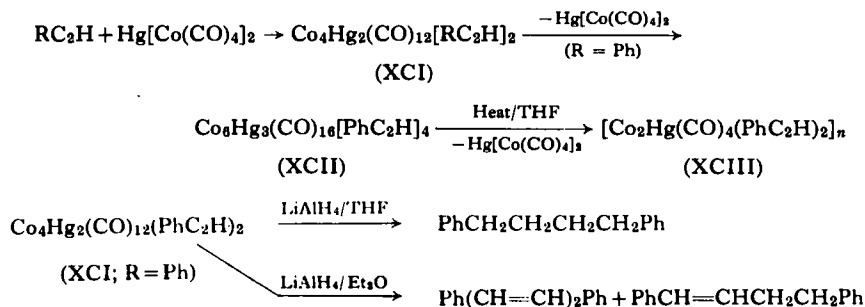
(LXXXIX)



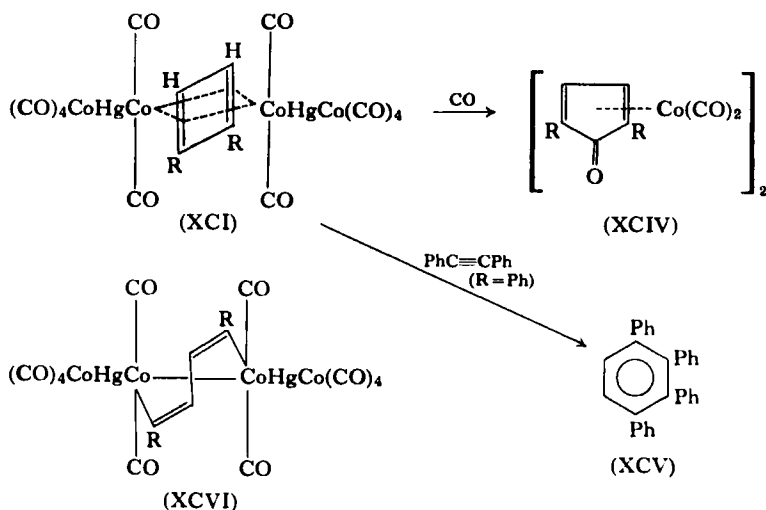
(XC)

Krüerke and Hübel (57) reported the isolation of some very complex products from the reaction of either *tert*-butylacetylene or phenylacetylene with mercury bis(cobalt tetracarbonyl). In each case one product analyzed correctly for  $Co_4Hg_2(CO)_{12}[RC_2H]_2$  (XCI) and the one where  $R = Ph$  disproportionated easily to give bis(cobalt tetracarbonyl)mercury and new

complexes (XCII) and (XCIII). These three complexes had very similar infrared spectra and hence it was postulated that all three had the same organic ligands and the same type of bonding.



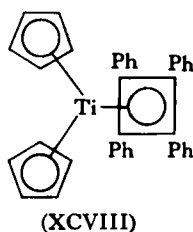
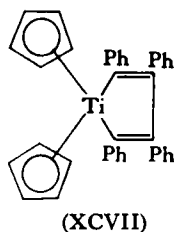
Lithium aluminum hydride reduction established that the organic ligand was an acetylenic tail-to-tail dimer, while bromination gave cyclopentanones, cyclopentenones, and cyclopentadienones with incorporation of CO. On this basis the authors proposed the complexes to have cyclobutadienes as ligands, e.g., (XCI).



Surprisingly, however, for compounds of such structure, reaction with CO at 80° C and 1-atm pressure gave 2,5-cyclopentadienonecobalt carbonyl complexes (XCIV), and reaction of (XCI; R = Ph) with diphenylacetylene gave 1,2,3,4-tetraphenylbenzene (XCV). In each case, therefore, attack

occurred at the *most* hindered side of the cyclobutadiene and with surprising facility in view of the general inertness of such complexes to this type of reaction. An alternative would be to formulate these as butadiene complexes, e.g., (XCVI) for (XCI). These would have the advantage of explaining the reaction products more easily. Further, a model of (XCVI) shows the cobalt atoms to be in contact, hence these complexes are expected to be diamagnetic with a metal-metal bond. In view of the ease with which diphenylacetylene will form tetraphenylcyclobutadiene complexes (Sections IV, B and IV, C) it would be very surprising if phenylacetylene and *tert*-butylacetylene were to form complexes of type (XCI) while diphenylacetylene did not. A somewhat analogous structure to (XCVI) has been shown to occur in a triacetylenedicobalt tetracarbonyl complex involving *tert*-butylacetylene (76).

Volpin *et al.* (92) reported that a mixture of sodium cyclopentadienide, titanium tetrachloride, and diphenylacetylene gave a derivative of bis(cyclopentadienyl)titanium for which they suggested structure (XCVII) or, less probably, (XCVIII).



Since Braye *et al.* (15) have prepared the zirconium analog of (XCVII) by an essentially similar route, (XCVII) is probably the correct structure. Its degradation with bromine to titanocene dibromide and a 1,4-dibromotetraphenylbutadiene also support this (92).

Tsutsui and Zeiss (90) showed that when diphenylacetylene was added to a solution of an unstable nickel(II) compound, dimesitylnickel, at low temperatures, an orange material with a composition close to that required for (diphenylacetylene)<sub>4</sub>Ni and hexaphenylbenzene were obtained. The orange material was quite intractable; hydrochloric acid removed the nickel to give an organic material which was also insoluble and intractable. The authors suggested that this might be a bis(tetraphenylcyclobutadiene)nickel, but insufficient evidence is available.

The only bis(cyclobutadiene)-metal complex so far described is the molybdenum one, (XXIII). The reason for the lack of other analogs of

ferrocene is not clear; however, synthetic difficulties may be partly responsible. The possible bonding in bis(cyclobutadiene)nickel has been discussed briefly by Fischer (39).

Some reports of failures to obtain cyclobutadiene complexes have also appeared (10, 40). Chatt *et al.* (21) also noted that biphenylene (II) was very reluctant to form a metal complex. The only ones which could be made were molybdenum tricarbonyl complexes where the  $\text{Mo}(\text{CO})_3$  group was bonded to the benzene, rather than to the four-membered ring.

## VIII

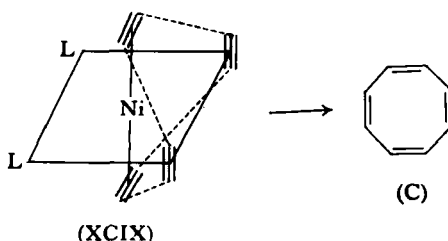
### CYCLOBUTADIENE-METAL COMPLEXES AS REACTION INTERMEDIATES

Bergmann in 1948 already had suggested that cyclooctatetraene may be formed in the Reppe synthesis by dimerization of cyclobutadiene (9). This suggestion was also put forward by Longuet-Higgins and Orgel (60) to account for the low yield of benzene in this reaction, since benzene, being more thermodynamically stable, would be the expected product. Schrauzer and his co-workers (86) in a careful study of the Reppe reaction found that the rate of formation of cyclooctatetraene (C) depended strongly on the nature of the nickel complex (being highest for kinetically labile complexes) and also on the solvent. Solvents of moderately high polarity were best; complexing solvents gave no cyclooctatetraene. In the presence of one mole of triphenylphosphine (a very strongly coordinating ligand) no cyclooctatetraene was formed, but benzene was obtained in high yield. Strong chelating ligands such as 2,2'-dipyridyl completely poisoned the catalyst. These results suggested that only complexes where four coordination positions around the octahedral nickel can be made available to the weakly coordinating acetylenes will act as catalysts for cyclooctatetraene formation. When one of these sites is blocked by a phosphine, only three remain and benzene is produced as a result.

Schrauzer *et al.* suggested that for cyclooctatetraene formation these four coordination positions are occupied by acetylenes which are thus automatically arranged (XCIX) in such a fashion that on coupling they give the cyclooctatetraene (C) and that a cyclobutadiene is not an intermediate.

On the other hand, a number of the presently known cyclobutadiene-metal complexes (as well as some reactions in which cyclobutadiene-metal

complexes may be intermediates) give tricyclooctadienes or cyclooctatetraenes under suitable conditions (3, 5, 28, 29, 38, 45, 72, 77, 87, 93) (see



Sections VI, A and VI, D). As very little information on the stabilities and modes of reaction of most cyclobutadiene-metal complexes is yet available, it is perhaps too early to be certain that under some conditions the tetramerization of acetylenes to cyclooctatetraenes does not occur via cyclobutadiene-metal complexes.

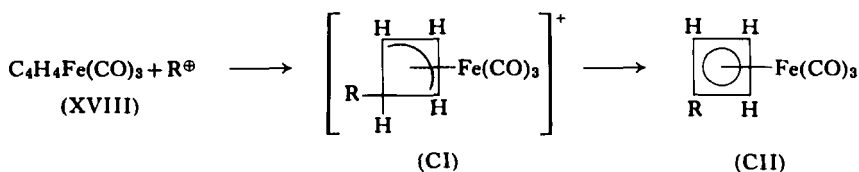
Cyclobutadiene-metal complexes have also been suggested as intermediates in a number of other reactions, notably in the formation of benzenes by trimerization of acetylenes (2, 18, 57, 90) and also in other reactions. Conclusive evidence is still lacking, but the inertness of the known cyclobutadiene complexes towards acetylenes in Diels-Alder type reactions makes this rather unlikely. Intermediates with open-chain structures such as (XCVI) appear more attractive. Arnett and Bollinger (2) have isolated by-products from the dicobalt-octacarbonyl-catalyzed trimerization of diisopropylacetylene which are very similar to some, e.g., (LI), obtained in the thermal decomposition of tetramethylcyclobutadienenickel chloride complexes (29). Again, here, however, the evidence is by no means conclusive and a variety of intermediates other than a cyclobutadiene-metal complex can be postulated to explain the observed products; however, see also the Appendix.

## IX

### APPENDIX

Some further important work on cyclobutadieneiron tricarbonyl which appeared too late for inclusion in the main text is included here since this gives the first clues to the behavior to be expected of unsubstituted cyclobutadiene complexes.

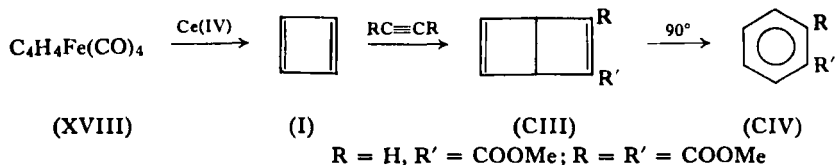
Pettit *et al.* (39a) have found that cyclobutadieneiron tricarbonyl (XVIII) undergoes electrophilic substitution under very mild conditions to give a variety of monosubstituted cyclobutadiene-iron tricarbonyls (CII; R = D, COCH<sub>3</sub>, CHO, CH<sub>2</sub>Cl, HgCl, CH<sub>2</sub>NMe<sub>2</sub>). The authors have suggested that the reactions proceed via cyclobutenyliron tricarbonyl cationic complexes (CI).



These reactions thus appear analogous to those of the substituted cyclobutadiene-nickel and -palladium halides with nucleophiles (Section VI, F).

Simple reactions on the substituents can also be performed without destroying the complexes. Thus the aldehyde (CII; R = CHO) undergoes borohydride reduction to the alcohol (CII; R = CH<sub>2</sub>OH), silver oxide oxidation to the acid (CII; R = COOH), and adds methyl magnesium bromide to give the secondary alcohol (CII; R = CHOHMe) after hydrolysis. The NMR spectra are consistent with their formulation as (CII) (see Section V, D). The complex (XVIII) thus behaves analogously to ferrocene and cyclopentadienylmanganese tricarbonyl.

Oxidation of (XVIII) with ceric nitrate gives a dimer of cyclobutadiene and other products (Section VI, C). In the presence of acetylenes the bicyclohexadienes (CIII) can be isolated; they isomerize to the benzenes (CIV) on heating.



The oxidation was also carried out under reduced pressure and the gaseous products collected in a cold receiver. After addition of methyl propiolate to the contents of the receiver, vapor-phase chromatography of the products showed the presence of a small amount of methyl benzoate (CIV; R = H, R' = COOMe). This result was interpreted to mean that

cyclobutadiene free from its metal complex is produced in these reactions and that it has a finite lifetime even though it is extremely reactive (92a). The mode of addition of cyclobutadiene with dienophiles suggests that the free cyclobutadiene is in a singlet, rather than a triplet state (82a).

Pettit *et al.* (82a) have also reported the preparation of tetramethylcyclobutadieneiron tricarbonyl and 1,2-diphenylcyclobutadieneiron tricarbonyl from the dihalocyclobutene and  $\text{Fe}_2(\text{CO})_9$  (Section IV, A).

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# Organoarsenic Chemistry

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## I

### INTRODUCTION

Apparently the first organic arsenic compound was obtained by Cadet de Glassicourt in 1760 when he heated arsenic trioxide with potassium acetate and obtained two immiscible liquids. The heavier liquid, spontaneously inflammable in air, became known as “Cadet’s fuming arsenical liquid.” It was studied by many chemists, including Bunsen, Berzelius, Frankland, and Cahours, about the middle of the next century, and was eventually shown to be tetramethyldiarsine (“cacodyl”). Since then many thousands of organic arsenic compounds have been prepared, most of them following the discovery by Ehrlich and his collaborators that certain arsenicals, notably 3,3′-diamino-4,4′-dihydroxyarsenobenzene (“Salvarsan,” “606,” “Arsphenamine”) were extremely effective against trypanosomes, spirillae, and spirochetes.

This review, however, is concerned with chemistry and not chemotherapy. It is concerned with the preparation and properties of compounds of

arsenic containing at least one carbon-to-arsenic bond, and, since arsenic can have a valency of 3 or 5, derivatives of the type  $R_nAsX_{3-n}$  ( $n = 1-3$ ) and  $R_nAsX_{5-n}$  ( $n = 1-5$ ). Complexes like  $[(C_2H_5)_3As]_2PtCl_2$  and  $(CH_3)_3AsBH_3$  are not included.

The complete literature on organic arsenicals up to 1929 is covered by three books (1, 2, 3), and since then at least three other books have devoted space to this topic (4, 5, 6). The last reference contains a noncritical compilation of information reported for the years 1937-1959. (A copy of it became available only after the present article was written). Heterocyclic derivatives are discussed in a book (7) and in a more recent review (8). Other articles have been concerned with the stereochemistry of arsenic (7, 9, 10), the preparation of Lewisite (11, 12), the search for chemotherapeutic agents (13), the preparation of aryl arsonic and arsinic acids (14), arsenic-containing derivatives of pyridine (15), and organoarsenical polymers (15a). Some more general articles have been published (16, 17, 17a). Because of the large number of organoarsenic compounds now known, and since most of these can be made by a variety of methods, no attempt has been made to provide tables of boiling points, melting points, and methods of preparation for individual compounds in this survey. Information of this sort is available in Krause and von Grosse (4), Dubb (6), and Kaufman (17b).

## II

### PREPARATIVE CHEMISTRY

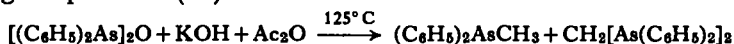
#### A. Formation of Arsenic-Carbon Bonds

##### 1. Cadet's Method

Methylarsines were first prepared by heating (300° C) arsenic trioxide with potassium acetate to give a mixture of tetramethyldiarsine (cacodyl), and bis(dimethylarsenic) oxide (cacodyl oxide). The method has been extended to produce other alkyl arsenicals (3, 18). It has been suggested as a semicontinuous means of preparing compounds of the type  $R_2AsCl$  and  $R_2As-AsR_2$ ; the chloride being produced by the action of ferric or mercuric chloride on the initial reaction products, and the diarsine by means of electrical reduction (19, 20).

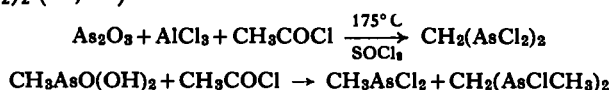
At lower temperatures (140°-175° C) heating arsenic trioxide with an aqueous solution of potassium carbonate, acetic anhydride, and acetic acid,

produces methylenedi(arsine oxide),  $[\text{CH}_2(\text{AsO})_2]$  (21). When bis(diphenylarsenic) oxide is used in a similar reaction, methylenebis(diphenylarsine) is among the products (22).



Note that in the last example a methyl group has also been transferred to the arsenic. Ethyldiphenylarsine can be made by this method.

Arsenic oxides also react with acyl chlorides, either alone or in the presence of aluminum trichloride, to give derivatives of the type  $\text{RCH}(\text{AsX}_2)_2$  (23, 24).



## 2. Reactions Using Elemental Arsenic

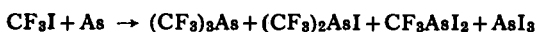
Cahours (25) found that heating methyl iodide with arsenic gives tetramethylarsonium iodide as the major product. More recent investigation has shown that other alkyl halides can be used, that copper can act as a catalyst, and that even bromobenzene and vinyl bromide react (26). The method has been developed as a means of preparing bromomethylarsines (27).



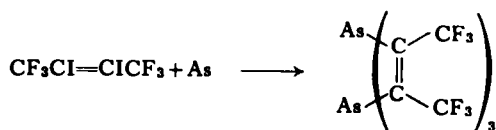
Iodoform reacts with arsenic to give products which, when oxidized with nitric acid, yield tetraiodocacodylic acid  $(\text{CHI}_2)_2\text{AsO}(\text{OH})$  (28). The initial reaction is probably as follows:



In the fluorocarbon field it was found that heating perfluoroalkyl iodides with arsenic gives a mixture of products (28a, 29, 30, 31).

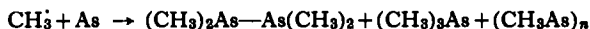


However, perfluoropropyl arsenicals seem to be difficult to isolate (32). Perhaps the most unusual product of this type of reaction is a bicyclo-octatriene (33).



It is probable that these reactions involve free radical attack on arsenic.

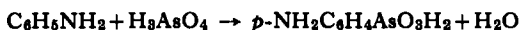
Paneth in his investigations of free radicals in the gaseous state used arsenic mirrors as detectors, and found that a mixture of products is obtained (34).



When a cold mirror is used the main product is the diarsine. It seems that methylene radicals also react with arsenic mirrors though in this case the products have not been identified (35). Phenylarsines are produced when phenyllithium or phenylmagnesium bromide react with arsenic (36), when phenyldiazonium chloride is decomposed by chalk in the presence of arsenic (37), and when tetraphenyltin is heated with arsenic (37a). These reactions are also believed to involve free radicals.

### 3. The Béchamp Reaction

Béchamp (38) obtained a colorless product on heating aniline arsenate with excess aniline. This was subsequently identified as an arsanilic acid.



The arsinic acid,  $(\text{NH}_2\text{C}_6\text{H}_4)_2\text{AsO}_2\text{H}$ , is also formed to a small extent (39). Literature up to 1944 is well covered in an article (14) which describes the arsonation of phenols, phenyl ethers, phenylamines,  $\alpha$ -naphthylamines (but not  $\beta$ -), and dibenzofuran. A pyridine derivative, 2-pyridinol, can also be arsonated in the 3- or 5-position by this method (40).

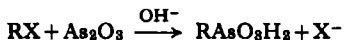
Since 1944 only a few applications of the Béchamp reaction have been made, one of the more interesting being the displacement reaction



claimed to give the arsonic acid in 90% yield (41).

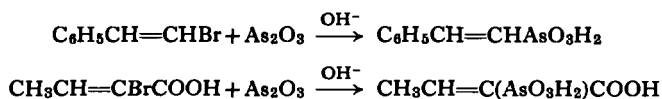
### 4. The Meyer Reaction

This reaction provides a convenient route for the preparation of aliphatic arsonic acids from sodium arsenite and alkyl halides (42).



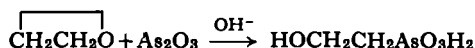
When applied to aromatic halides the reaction is known as the Rosenmund reaction, but few successful preparations of this type have been reported (14). The general conditions have been studied (43, 44) and it has been found (44) that arsonation of primary aliphatic halides proceeds smoothly, secondary aliphatic halides are arsonated only with difficulty, and tertiary not at all.

Substituted halides are said to react depending on the position and nature of the substituents. For example  $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{Cl}$  does not react, yet the corresponding bromide does. Allyl halides react, vinyl halides do not. Substituted vinyl halides, however, do react (45, 46).

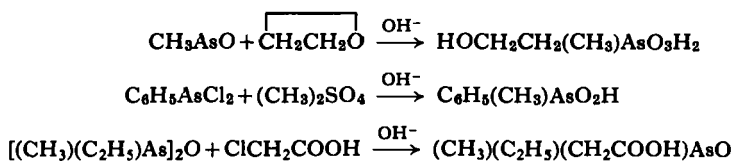


The last example is of interest since it is claimed that the same isomer is formed from both *cis* and *trans* bromides. A similar situation apparently occurs in the arsonation of isomers of  $\text{CH}_3\text{CCl}=\text{CHCOOH}$  (46).

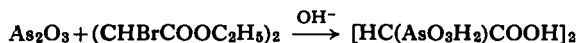
The alkyl halide can be replaced by alkyl sulfates (47, 48, 49) and by ethylene oxides. In the latter case  $\beta$ -hydroxyalkyl derivatives are obtained (50).



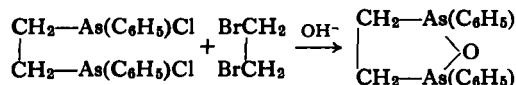
The Meyer reaction can be used to bond a second or even a third alkyl group to an arsenic atom (49, 51, 52).



There may be some doubt about the last example. Replacement of two halogens in the same molecule is possible (53, 54, 55).

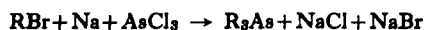


However, attempts to use disubstitution to obtain cyclic derivatives have not been successful, only the hydrolysis product being isolated (56).



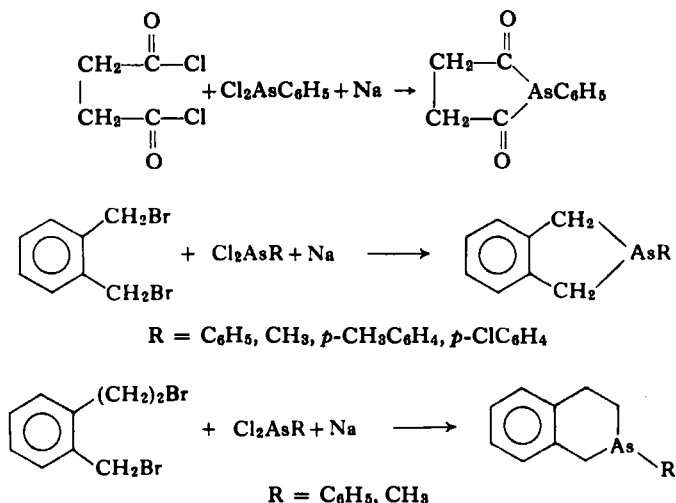
### 5. The Wurtz-Fittig Reaction

This reaction is also known as the Michaelis condensation because of its early use by Michaelis and his co-workers to prepare triarylsarsines (57).

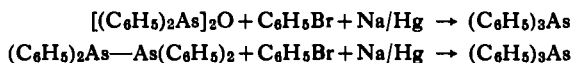


Reaction is usually carried out in benzene or ether, and often needs to be catalyzed by ethyl acetate. Only one trialkylarsine  $[(C_3H_7)_3As]$  seems to have been synthesized by this method (58).

In recent years the reaction has been used to prepare tri(biphenyl)-arsines (59), tri( $\beta$ -phenylvinyl)arsine (45), and some cyclic arsines (60–63).

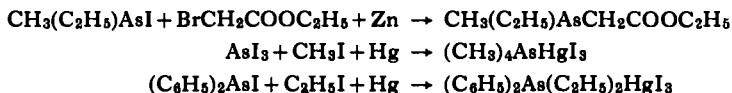


Arsenic oxides and diarsines have also been used in this type of reaction (64).

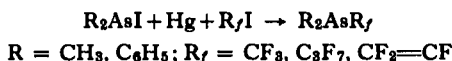


Although the mechanism of the normal type of Wurtz-Fittig reaction is not known, there being many possibilities, there is evidence that intermediates containing As—Na bonds are involved in the last two examples.

Zinc, magnesium, and mercury have also been used to effect coupling (65, 66).



When iodoarsines are coupled with fluorocarbon iodides in the presence of mercury, arsines and not arsonium derivatives are produced (67–70).





However, some unexpected products can be obtained from this type of reaction (69) viz.,



There is considerable evidence indicating that these reactions proceed through intermediates containing As—Hg bonds (70, 71).

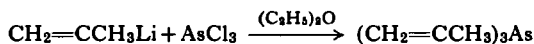
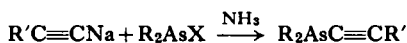
### 6. Reaction of Arsenic Compounds with Organometallic Compounds

This type of reaction was first used in the arsenic field for the preparation of aryldichloroarsines (57, 72).

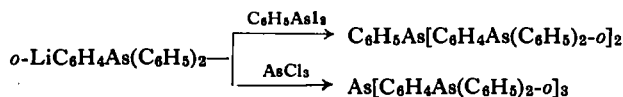
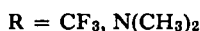
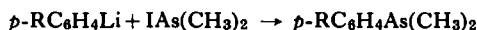
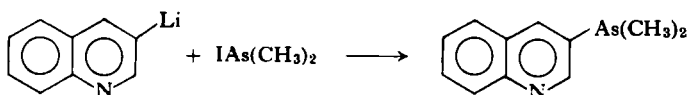


Trialkylarsines were first obtained from zinc alkyls (73).

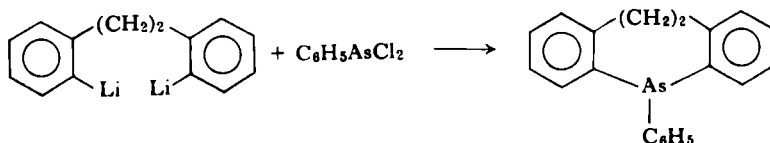
a. *Reaction with Compounds of Group I.* Sodium and lithium compounds have been used to prepare a number of derivatives of acetylenes and olefins (74, 75).



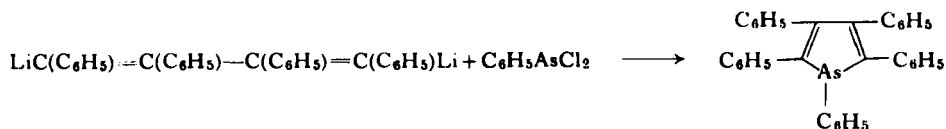
The *cis* and *trans* isomers of  $(\text{CH}_3\text{CH}=\text{CH})_3\text{As}$  can also be obtained from similar reactions (75). Lithium derivatives have yielded aromatic arsenicals (76–80).



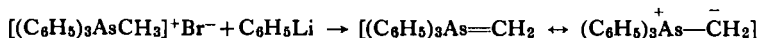
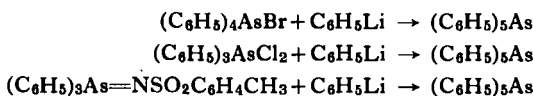
The last example involves the synthesis of two new important polydentate ligands. In the heterocyclic field lithium derivatives have been used to good effect (81, 82).



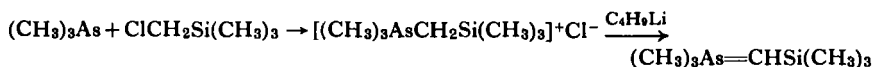
Perhaps the most interesting reaction affords pentaphenylarsole (83, 84).



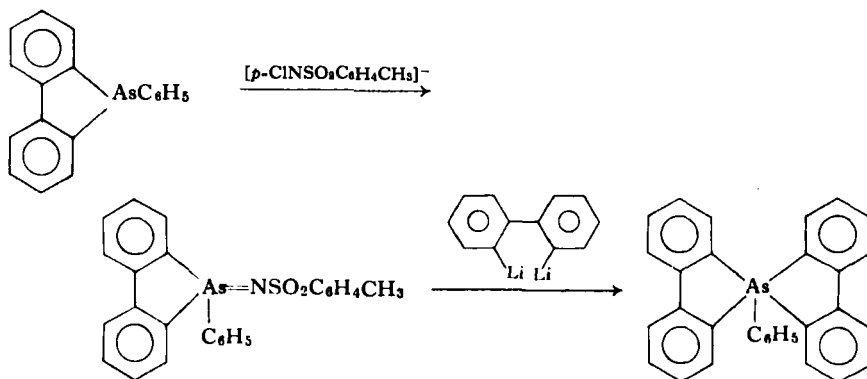
The most significant recent development in arsenic chemistry has been the preparation of compounds like pentaphenylarsenic and triphenylarsine-methylene (85-88).



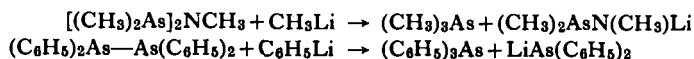
A volatile trimethylsilyl containing ylid [b.p. 69°C (6 mm)], has been isolated (88a).



It is possible that pentaalkyl arsenic compounds might be formed from similar reactions (89, 90). Pentamethylarsenic was in fact claimed to exist as early as 1862 (91). Wittig and Hellwinkel have prepared spiro arsenicals related to pentaphenylarsenic by this type of reaction (86).



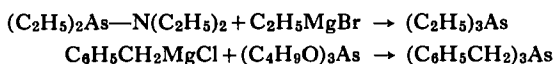
Compounds with As—N and As—As bonds are cleaved by lithium alkyls and aryls (91a, 91b, 91c).



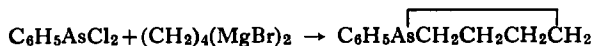
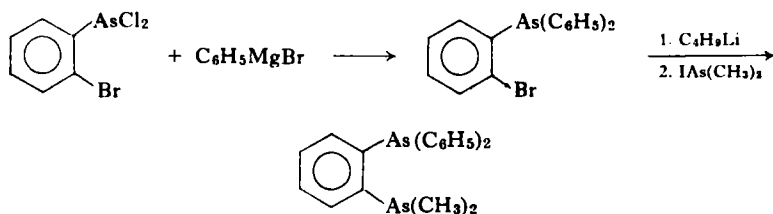
b. *Reaction with Compounds of Group II.* The reaction between Grignard reagents and arsenic halides has long been used as a means of preparing both alkyl and arylarsines (3). It was also found that arsenic oxides would react similarly (92, 93), and Blicke and co-workers were able to prepare tetra-arylarsonium salts by this method (64, 94, 95).



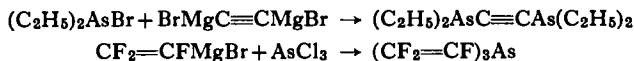
Alkoxides and even amino derivatives also react with Grignard reagents (96, 97).



The more usual Grignard procedure using haloarsines has been used to prepare a host of trialkylarsines and mixed alkylarsines of the type  $(\text{CH}_3)_2\text{AsC}_6\text{H}_{11}$  (98, 99) although even this has recently been modified, the reactions being carried out in nonethereal media such as iso-octane (100). Tris(trimethylsilylmethyl)arsine,  $[(\text{CH}_3)_3\text{SiCH}_2]_3\text{As}$ , has been prepared from  $(\text{CH}_3)_3\text{SiCH}_2\text{MgCl}$  using standard procedures (101). The synthesis of bi- and tridentate chelating agents and cyclic arsines has also been achieved by similar means (7, 102, 103).



Synthesis of vinyl, allyl, ethynyl, and perfluorophenylarsines has been similarly accomplished (45, 104–109, 109a).



As a corollary, it has been suggested that a useful way of identifying the products formed from the interaction of magnesium with aromatic dihalides is to treat the resulting mixture with iododimethylarsine and work up the resulting arsines (110).

As mentioned above, reaction of haloarsines with zinc dialkyls or mercury diaryls has been a useful method of forming As—C bonds. In recent years the

use of zinc compounds has been largely superseded by the more accessible Grignard and lithium reagents. Nevertheless, certain arsines have been prepared by way of the mercury intermediate. In the aromatic field Blicke and Smith (93) used the reaction as a means of preparing aryldichloroarsines as did Drefahl and Strang more recently (111).

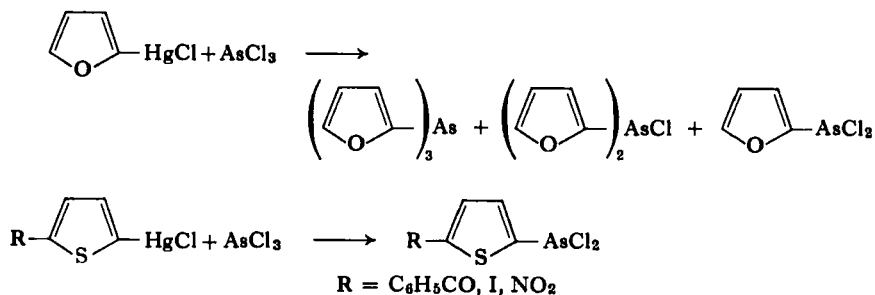


Treatment of phenylmercury chloride with arsenic trichloride has been suggested as an industrial method for preparing chlorodiphenylarsine (112). However, Mann and Watson found that the mercurial method was not good for the preparation of aromatic arsenicals of the type  $\text{ArAr}'\text{AsCl}$  by the reaction

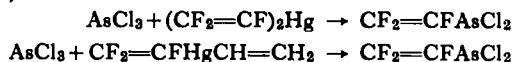


They obtained mainly  $\text{Ar}_2\text{AsCl}$  (113).

The main application of mercury derivatives has been to the synthesis of heterocyclic arsenicals. Thus diphenylene oxide-1-arsonic acid and pyridyl-3-arsonic acid have been isolated following oxidation of the initial reaction products obtained from arsenic trichloride and the appropriate heterocyclic mercury chloride (114, 115). Furan and thiophene derivatives have been similarly prepared (116, 117, 118).



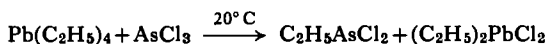
The furan reaction was shown to be an equilibrium, and to be catalyzed by mercuric chloride (116). Tris(2-furyl)arsine has also been prepared by Wurtz-Fittig and Grignard procedures (119). The most recent use of mercury compounds has been in the preparation of dichloroperfluorovinylarsine (120, 121).



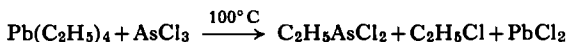
It is worth noting that the perfluorovinyl group can be transferred from mercury to arsenic whereas the trifluoromethyl group cannot (122, 123).

c. *Reaction with Compounds of Group III.* So far only aluminum alkyls have been studied and it has been claimed that these react with arsenic halides, oxides, or sulfides, yielding trialkylarsines (124). Later work, however, suggests that alkylation of  $\text{As}_2\text{O}_3$  with  $\text{AlR}_3$  ( $\text{R} \geq \text{C}_4$ ) affords mainly bis(dialkylarsenic) oxides  $[(\text{R}_2\text{As})_2\text{O}]$  (125). Lithium tetraethylaluminate ethylates arsenic trichloride giving triethylarsine (126).

d. *Reaction with Compounds of Group IV.* The first main study in this area was made by Kharasch *et al.* (127). They found that tetraethylead and arsenic trichloride react spontaneously, giving dichloroethylarsine.



At  $100^\circ\text{C}$  the reaction is more efficient, and at  $120^\circ\text{C}$  chlorodiethylarsine is formed.

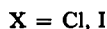
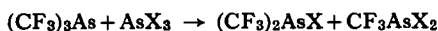
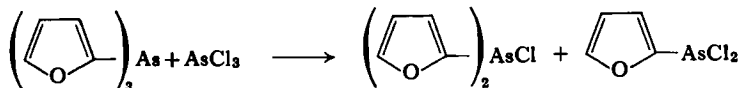


Kamai and Gatilov have since made use of this reaction to prepare arsines of the type  $(\text{C}_2\text{H}_5)_2\text{RAsCl}$  from  $\text{RAsCl}_2$  (128, 129).

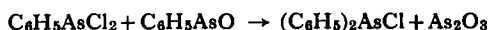
Tin compounds can also be used; one of the more interesting examples involves the transfer of vinyl groups from tin to arsenic (106).



e. *Reaction with Compounds of Group V.* As mentioned earlier, reaction of triarylarsines with arsenic trihalides was once a convenient source of arylchloroarsines. However, in the aromatic field there has been very little occasion to use this method recently, since more convenient methods of synthesis are now available. The reaction, nevertheless, has been of use in the synthesis of other haloarsines (29, 106, 116, 130).

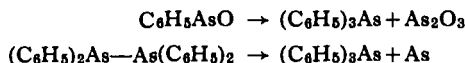


A somewhat similar reaction is the following:

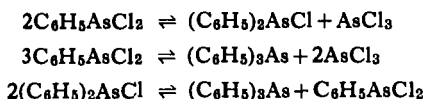


This process is catalyzed by zinc oxide, and has been investigated as a means of producing chlorodiphenylarsine on a large scale (131).

Disproportionation reactions also afford new As—C bonds and there are a number of such examples in the older literature, for example (3),



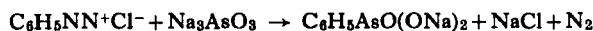
Similar and more recent examples are known (71, 132). The decomposition of phenyldichloroarsine in the liquid state can be represented by a series of equilibria (133).



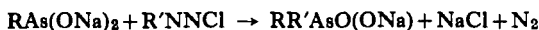
The main reaction in the region 220°–338° C is represented by the first equation. Similar equilibria seem to occur in related reactions.

### 7. The Bart Reaction

The original method consisted of coupling an alkali arsenite with a diazotized amine to give, after loss of nitrogen, aromatic arsonic acids.



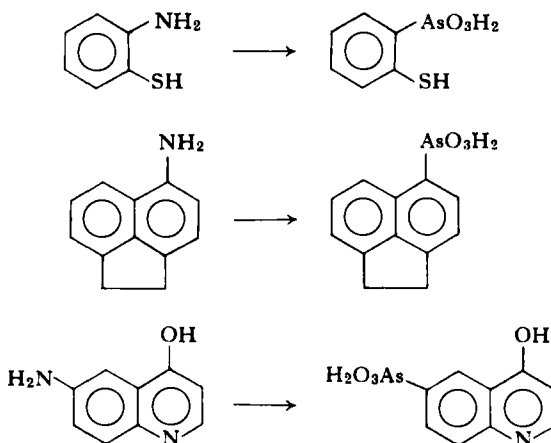
Arsinic acids and even arsine oxides can also be obtained by this procedure.



It has been found that certain metals and metallic salts catalyze the reaction and that neutral or even acid conditions can be used. The literature up to 1944 is well reviewed in an article which also includes some sample preparations (14).

Since 1944, as before, the Bart reaction has been the main method used for preparing aromatic arsenicals. In spite of this no definitive studies have been made. It has been found that OH or NO<sub>2</sub> groups *ortho* or *para* to the diazo group facilitate coupling (134), and that small amounts of compounds containing two and even three aromatic groups per arsenic atom are produced from secondary reactions (135).

The following examples should give some idea of recent applications (136, 137, 138):



In addition, polymers such as poly(4-aminostyrene) have been arsonated by this method (139).

An important modification of the original Bart procedure was made by Scheller who diazotized primary amines, dissolved in alcohol or glacial acetic acid, in the presence of arsenic trichloride and found that better yields of arsonic acids could sometimes be obtained, particularly if the amine carried negative substituents in the *meta* position. The method has been slightly modified (140). The Scheller reaction has recently been used to prepare arsonic acids of 3-nitro-4-fluorobenzene and 2,5-dimethylpyridine (141, 142), and to prepare a number of arsinic acids such as  $(\text{C}_6\text{H}_5)_3\text{AsO}_2\text{H}$  by the reaction (143)

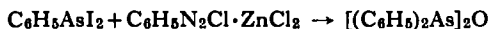


Another early development of the Bart procedure was the use of diazonium fluoroborates instead of the more usual chlorides (144, 145). Subsequently Doak and Freedman (146) found that dry diazonium fluoroborates react with arsenic trichloride in dry ethanol to give both arsonic and arsinic acids. Under these conditions maximum yields of the arsonic acid are obtained using a cuprous chloride catalyst. In 80% ethanol quite high yields of the arsinic acid are obtained using cuprous bromide as catalyst. These workers later found that fluoro-zincates and fluoro-silicates give similar results (147).

Hanby and Waters (148) had earlier found that when dry diazonium chlorides or chlorozincates in acetone are decomposed with zinc dust in the presence of chloroarsines, triarylarsines are obtained.

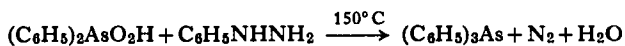


Similar reactions using tetrachloroferrates, arsenic trichloride, and iron powder yield, after hydrolysis, compounds of the type  $\text{ArAsO}$  and  $(\text{Ar}_2\text{As})_2\text{O}$  (149), and by using reactions such as



this procedure has been extended to the preparation of the oxides  $(\text{ArAr}'\text{As})_2\text{O}$  (150). Arylazocarboxylic salts like  $\text{C}_6\text{H}_5\text{N}_2\text{COOK}$  have been found to give similar products with haloarsines (151).

A related synthesis of aryl arsenicals involves the use of arylhydrazines as arylating agents (152–155).



The second reaction goes best with a cuprous oxide catalyst. This method, which probably involves diazonium intermediates, can be used to prepare substituted aromatic arsenicals such as  $(4\text{-ClC}_6\text{H}_4)_2\text{AsCl}$ . It has also been found that air oxidation of a mixture of arsenic trichloride and an arylhydrazine in the presence of cupric chloride results in the formation of aryl arsenicals (156).

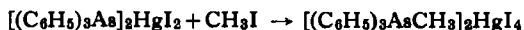
#### 8. Action of Alkyl, Aryl, or Fluoroalkyl Halides on Arsenic Compounds

a. *With  $\text{R}_3\text{As}$  to Produce Arsonium Derivatives.* The reaction of alkyl halides with trialkylarsines to produce tetraalkylarsonium halides has been known for over 100 years (3). In general, alkyl bromides or iodides interact easily with trialkylarsines, although as more negative groups such as phenyl or trifluoromethyl are substituted for the alkyl groups on the arsine, ease of reaction decreases. There have been only a few attempts made to evaluate the factors affecting arsonium salt formation (157, 158).

Although aryl halides do not normally add to arsines, Chatt and Mann (159) found that bromobenzene and triphenylarsine yield, in the presence of aluminum trichloride, the tetraphenylarsonium ion. The reaction is believed to proceed by addition to an initially formed 1:1 complex (160).



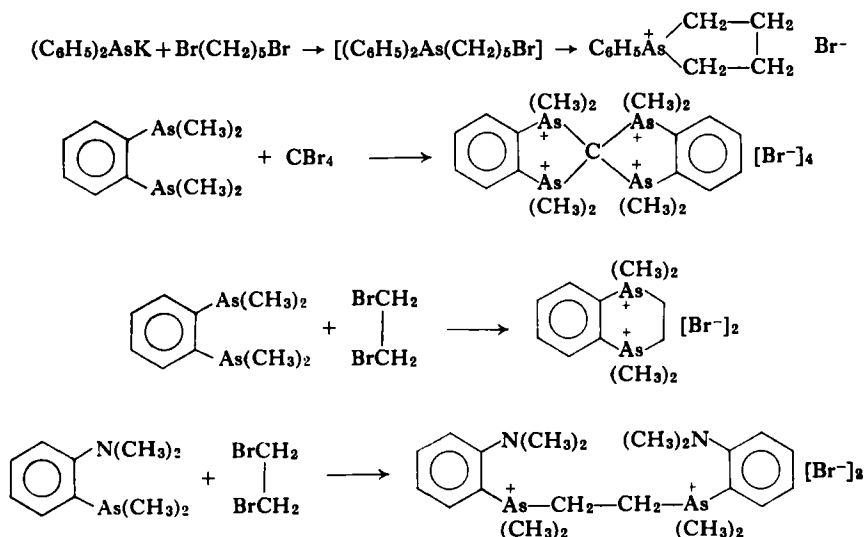
It has been used to prepare compounds of the type  $\text{ArAr}'\text{Ar}''\text{Ar}'''\text{As}^+\text{X}^-$  from  $\text{ArAr}'\text{Ar}''\text{As}$  (113). A somewhat similar situation is found in the reaction



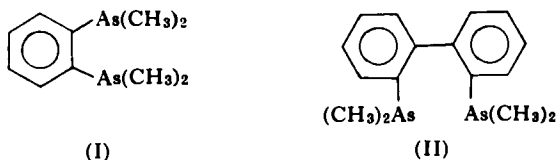


This occurs readily at 20°C, even though triphenylarsine and methyl iodide react only slowly, if at all, at this temperature (161).

In the 1930's there was great interest in the preparation of simple arsonium compounds, notably by Blicke and his co-workers (e.g., ref. 162), but since then interest has centered on the preparation of cyclic derivatives and the study of inductive deactivation. In both cases compounds with more than one potential onium group have been investigated (163–166).

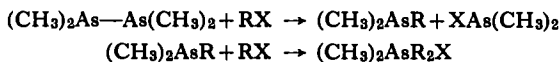


Methyl iodide reacts easily with one arsenic atom of compound (I) to give the monomethiodide, but much more forcing conditions are required to prepare the dimethiodide (165). In a similar way there is some difficulty in obtaining the dimethiodide of compound (II). However the deactivating effect of one  $-\text{As}(\text{CH}_3)_3^+$  group seems to be less in the case of the biphenyl derivative.

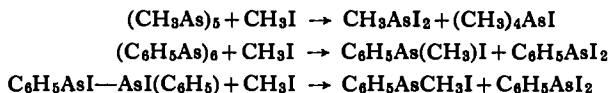


Possibly this is because the effect is over a greater distance (79). Other examples of inductive deactivation have been discussed (167).

b. *With Compounds Containing As—As Bonds.* Cahours and Riche (168) found that tetramethyldiarsine reacts with alkyl halides according to the equations



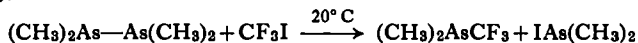
Steinkopf and co-workers (169, 170) also investigated this and related reactions and found that cleavage of the As—As bond was quite general.



Johnson investigated similar reactions in the phenarsazine series (171)



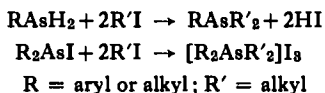
and found that when R = H cleavage at 100° C is facile, but when R = CH<sub>3</sub>CO then there is no reaction after several hours at this temperature. Trifluoriodomethane cleaves the As—As bond of tetramethyldiarsine at 20° C (67),



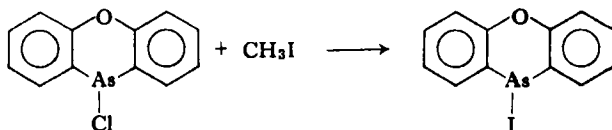
although the perfluoro compound, (CF<sub>3</sub>)<sub>2</sub>As—As(CF<sub>3</sub>)<sub>2</sub>, requires higher temperatures. Arsenobenzene is also cleaved by trifluoriodomethane either on heating or on ultraviolet irradiation (70).



c. *With Other Arsenic Compounds.* Alkyl halides usually react with arsenicals containing As—H or As—X bonds (X = halogen) replacing the hydrogen or halogen with an alkyl group (3).



No recent examples of this type of reaction have been reported. However some exceptions have been found in the heterocyclic field (172).



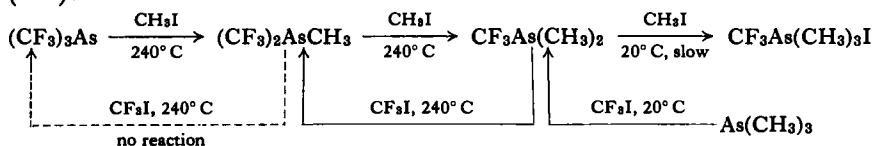
Tris(trifluoromethyl)arsine does not form a stable arsonium iodide, although with methyl iodide the two compounds do appear to interact sufficiently to form an azeotropic mixture (173). At higher temperatures, or on ultraviolet irradiation, replacement of  $\text{CF}_3$  by  $\text{CH}_3$  occurs (30).



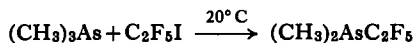
A related exchange reaction which proceeds even at  $20^\circ \text{C}$  was discovered by Haszeldine and West (174).



Their results and those of previous workers can be summarized as follows (175):



Other trialkylarsines and fluorocarbon iodides have been found to behave similarly (176, 177).



The lower temperature reactions are believed to involve arsonium intermediates (175, 176, 177). At higher temperatures ( $> 170^\circ \text{C}$ ) even haloarsines and phenylmethylarsines react with trifluoriodomethane giving mixtures of products.

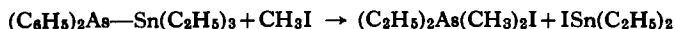


These are probably formed by free radical attack (176).

Cleavage of As—As bonds by fluorocarbon iodides has already been described above. A related reaction is the cleavage of As—S bonds (178).



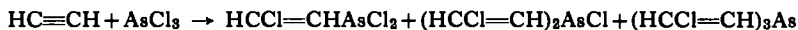
It is worth noting that under the same conditions the arsenic sulfides  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_6$  do not react. Cleavage of As—Sn bonds by methyl iodide has been reported recently (178a).



## 9. As—C Bonds Formed by Addition Reactions

### a. Addition of Olefins and Acetylenes to As—X Bonds

(i)  $X = Cl$ . Acetylene and arsenic trichloride react in the presence of aluminum trichloride to give a mixture known as "Lewisite" (11, 12, 179).

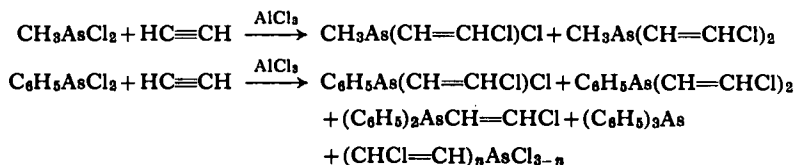


The main product is  $\beta$ -chlorovinylchloroarsine with the *trans* isomer predominating. The proportion of the *cis* isomer is increased when other catalysts such as mercuric and cuprous chloride are used (180, 181, 182), though this is never very great. The Lewisite phase usually separates from the reaction mixture and this is believed to be the reason for the predominant formation of the dichloroarsine. If acetone is added to the reaction mixture separation of the Lewisite layer does not take place, and the main product is tris- $\beta$ -chlorovinylarsine (181). Mercuric-chloride-catalyzed addition appears to proceed through a mercurial intermediate (181).

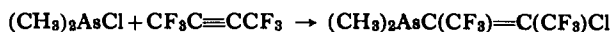


Probably aluminum trichloride catalysis is similar, although a different interpretation of both reactions has been offered (183).

Acetylene has also been added to compounds of the type  $RAsCl_2$  ( $R = CH_3, C_6H_5$ ) (184, 185).

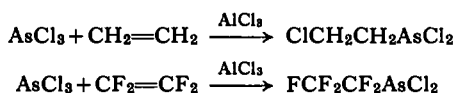


In the former reaction the main product is chloro( $\beta$ -chlorovinyl)methylarsine. In the latter triphenylarsine is produced in low yield together with traces of the compounds  $(CHCl=CH)_nAsCl_{3-n}$ , and the remaining phenylarsines are produced in approximately equal amounts. The aluminum trichloride catalyst probably also helps the redistribution reactions (see Section II, A, 6,e). Long-chain acetylene derivatives also react with chloroarsines in the same way (3, 186), but complex products are obtained from tetrolic acid and arsenic trichloride (187). Hexafluorobut-2-yne does not react with arsenic trichloride although it does so with chlorodimethylarsine on heating or ultraviolet irradiation (188).



The latter method is best, and the product is mainly the *trans* isomer. Heating gives a mixture of products and heating in the presence of aluminum trichloride gives a product in which the terminal chlorine is replaced by a fluorine. Other chloroarsines are surprisingly inert to hexafluorobut-2-yne (188).

The reaction of olefins with chloroarsines has had little attention. Arsenic trichloride and ethylene produce mainly  $\beta$ -chloroethyldichloroarsine (189) although further substitution may take place.



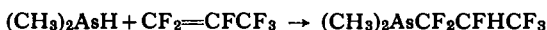
However, with tetrafluoroethylene, dichloropentafluoroethylarsine is the main product (190). Note that here again terminal chlorine has been replaced by fluorine.

(ii)  $X = H$ . Mann and his co-workers have found that many compounds containing As—H bonds add smoothly to acrylonitrile (191, 192, 193).

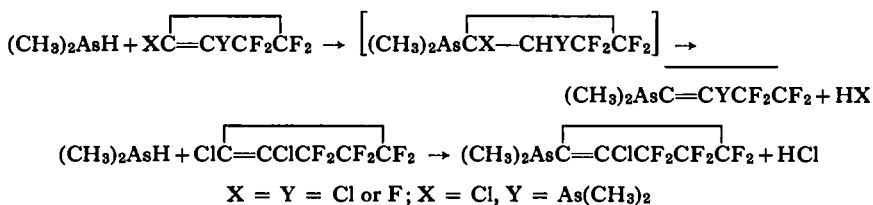


The reactions are base-catalyzed.

Dimethylarsine adds smoothly to hexafluoropropene (194).



With cyclic fluoroolefins the products seem to arise by addition of the arsenic hydride followed by elimination of hydrogen halide (194, 195).



These reactions proceed quite smoothly on heating. The yields can be very high. Elimination from the adduct is a function of the olefin since the hexafluoropropene adduct described above is stable to prolonged heating at 180° C (195).

Addition of arsenic hydrides to acetylenes has also been investigated to a limited extent. Dimethylarsine reacts violently with hexafluorobut-2-yne giving the expected butene derivative. The product is predominantly the

*trans* isomer. Methylphenylarsine reacts more slowly, and bis(trifluoromethyl)arsine requires strong heating to make the reaction go (196).

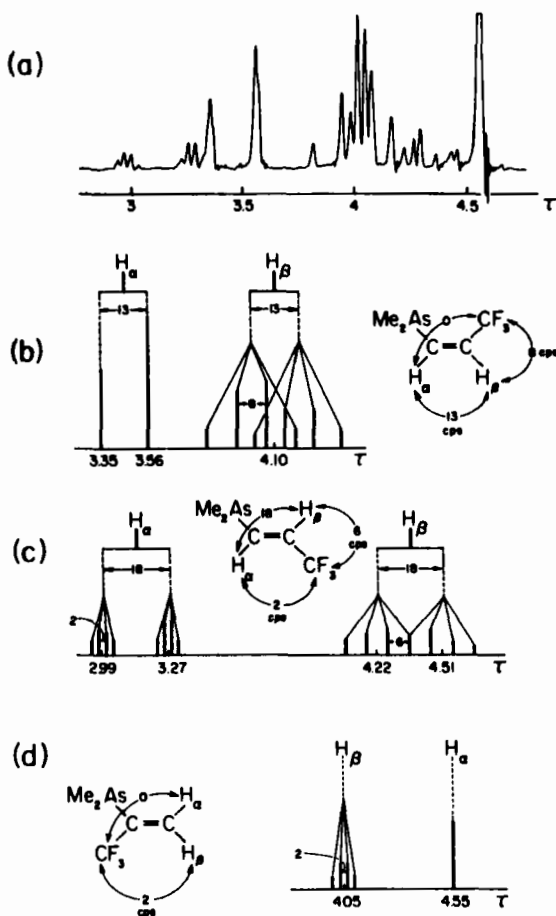


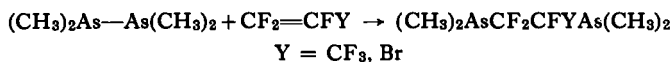
FIG. 1. Downfield  $^1H$  NMR spectrum of the products from the reaction of  $(CH_3)_2AsH$  with  $CF_3C\equiv CH$ .

Dimethylarsine and 3,3,3-trifluoropropyne afford a mixture of products. The isomer distribution from the room-temperature reaction is approximately *cis:trans:iso* = 3:3:2, as determined by NMR spectroscopy (196).

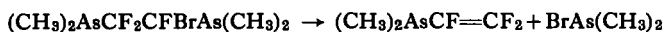


Figure 1 shows the downfield region of the spectrum of this reaction mixture and the contribution made by each isomer.

(iii)  $X = AsR_2$ . Tetramethyldiarsine adds to fluoroolefins under mild conditions, yielding 1:1 adducts (70).

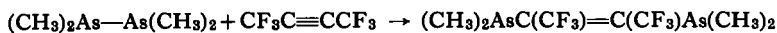


When  $Y = Br$  the adduct slowly decomposes at 20° C, affording dimethylperfluorovinylarsine and presumably bromodimethylarsine.



When  $Y = I$  an intermediate 1:1 adduct does not seem to be produced, and the reaction gives the perfluorovinylarsine directly. Thus this is analogous to the cleavage reactions described in Section II, A, 8,b. When  $Y = F$  the main product from the UV-irradiated mixture is the 1:4 adduct,  $(CH_3)_2As(CF_2CF_2)_4As(CH_3)_2$ .

Tetramethyldiarsine and hexafluorobut-2-yne also give a 1:1 adduct consisting of an approximately equimolar mixture of the *cis* and *trans* isomers (70).

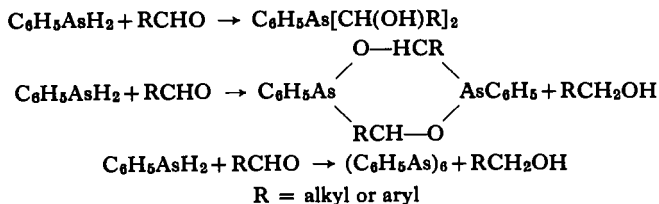


The butyne is much less reactive towards tetrakis(trifluoromethyl)diarsine; however, a 1:1 adduct is slowly formed on ultraviolet irradiation (188). Tetramethyldiarsine and 3,3,3-trifluoropropyne afford different products (197).



#### b. Other Addition Reactions

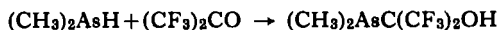
(i) *Addition of aldehydes and ketones to As—H bonds.* Adams and Palmer (198) found that aldehydes react with phenylarsine in three ways, depending on conditions.



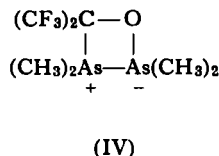
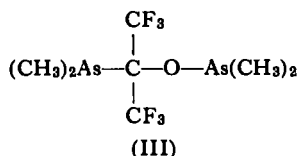
Adduct formation takes place at low temperatures and is catalyzed by hydrochloric acid and hydrogen chloride. Arsenobenzene is obtained from

uncatalyzed reactions at higher temperatures. The bis( $\alpha$ -hydroxyalkyl)-arsines are converted to tetrahydro-1,4,2,5-dioxadiarsine derivatives by reaction with alcohol-removing agents such as acetic anhydride.

Hexafluoroacetone also adds easily to dimethylarsine giving the  $\alpha$ -hydroxy derivative (199).

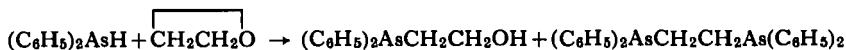


Some reduction to the secondary alcohol,  $(\text{CF}_3)_2\text{CHOH}$ , also occurs as a side reaction. The reaction of hexafluoroacetone with methylarsine is more complex. It might be expected that tetramethyldiarsine and hexafluoroacetone would yield compound (III), however, this is not so



and it appears that an easily dissociated complex is formed in which the As—As bond is retained (IV) (199). It reacts with water to liberate tetramethyldiarsine and with hexafluorobut-2-yne, a high yield of the 1:1 adduct,  $(\text{CH}_3)_2\text{AsC}(\text{CF}_3)=\text{C}(\text{CF}_3)\text{As}(\text{CH}_3)_2$ , is obtained [see Section II, A, 9,a]. However, in this case the adduct is predominantly the *cis* isomer (> 90%).

(ii) *Addition of ethylene oxide and its derivatives to As—H bonds.* Although many unsuccessful attempts have been made to react arsine itself with ethylene oxide, diphenylarsine does so on heating to 130° C to give a mixture of products including the expected 2-hydroxyethylarsine. The 1,2-bis(diphenylarsino)ethane is produced in appreciable amounts (200).



(iii) *Addition of methylene to As—Cl bonds.* Diazomethane reacts readily with arsenic trichloride in ether solution in the absence of catalyst (201), and the method has been extended to treating arsenic trichloride with methyl diazomethane (202).



Cookson and Mann tried a similar reaction using chlorodiphenylarsine and diazomethane and obtained the monoxide of methylenebis(diphenylarsine) as a major product (25% yield) (203). They did not

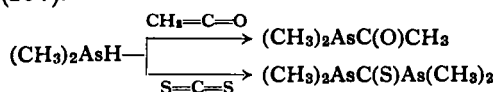


isolate any of the expected chloromethyl derivative, and suggested that the methylene compound was formed by attack of the diazomethane on the oxide  $[(C_6H_5)_2As]_2O$ .



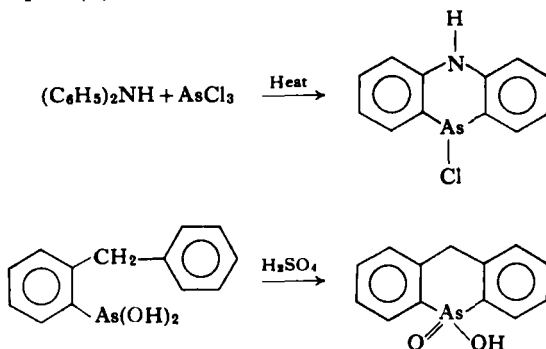
The oxide is presumably produced by hydrolysis of the chloride. If this interpretation is correct then the reaction seems to be worth further study.

(iv) *Addition of dimethylarsine to ketene and carbon disulfide.* The reaction with ketene goes as expected, producing the acetylarsine. However, with carbon disulfide 2 moles of the arsine react to give the thioketone  $[(CH_3)_2As]_2CS$  (204).

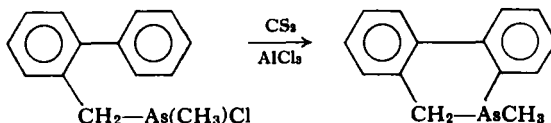


### 10. Elimination of Hydrogen Halide and of Water

This method had early use as a means of preparing cyclic arsines as in the following examples (7):



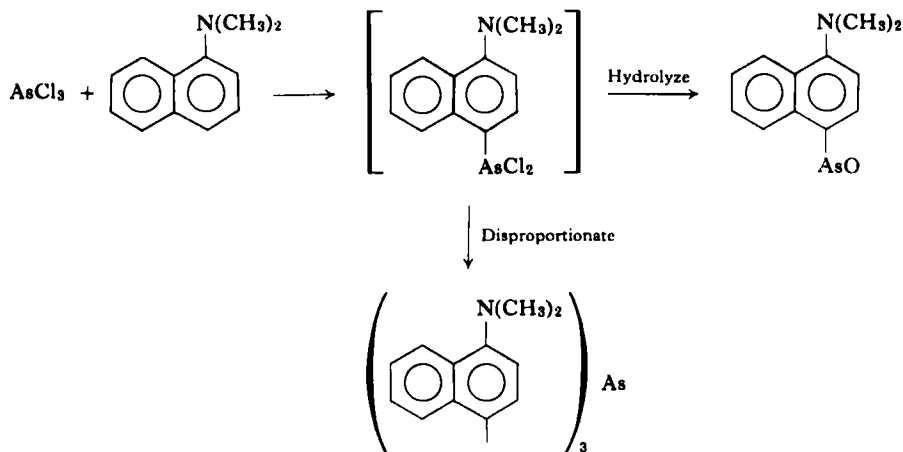
Sometimes cyclization requires a Friedel-Crafts catalyst such as aluminum trichloride (205).



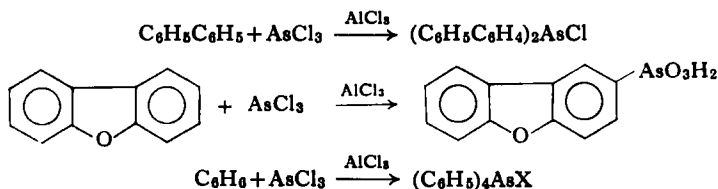
Mole and Turner (205a) have studied the effects of substituents on the rates of hydrogen chloride elimination to produce 10-chlorophenoxarsines.

In contrast with the above reaction of arsenic trichloride with diphenylamine, reaction with dimethylaniline occurs readily at ordinary temperatures

yielding tris(*p*-dimethylaminophenyl)arsine, [*p*-(CH<sub>3</sub>)<sub>2</sub>NC<sub>6</sub>H<sub>4</sub>]<sub>3</sub>As, (206). This product probably arises by disproportionation of an initially formed dichloroarsine. Related products have been isolated from similar reactions (207).

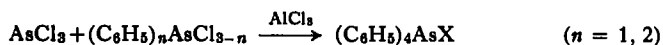


In the absence of dialkylamino groups, arsenation of aromatic systems is more difficult, requiring both heat and catalyst, for example (115, 159, 208),

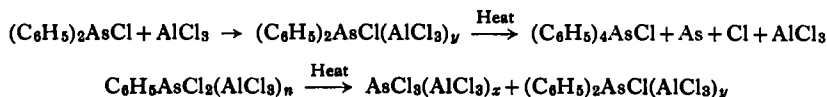


In the first reaction it is believed that substitution takes place in the *ortho* position and in the third, the nature of X, which is usually I<sup>-</sup>, depends on the work up. This catalyzed reaction has also been suggested as a means of preparing C<sub>6</sub>H<sub>5</sub>AsH<sub>2</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsH commercially (209).

Chatt and Mann found that the tetraphenylarsonium ion could also be obtained from chlorophenylarsines (159).

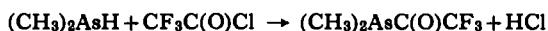
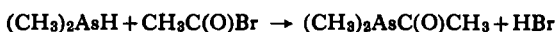


A mechanism has been suggested for these two reactions (160).



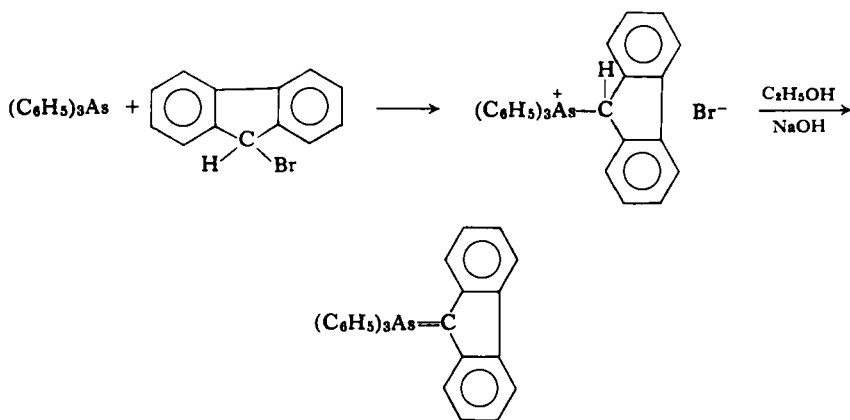
The latter reaction is essentially a catalyzed disproportionation (See Section II, A, 6,e). Thus, when benzene is arsenated with arsenic trichloride in the presence of aluminum trichloride, dichlorophenylarsine is probably first produced. The other reactions then take place to give the tetraphenylarsonium compounds.<sup>1</sup> Ferrocene and arsenic trichloride under Friedel-Crafts conditions afford only monosubstitution on arsenic (209a). Chlorodimethylarsine and 3,3,3-trifluoropropyne on heating yield the propynylarsine,  $(\text{CH}_3)_2\text{AsC}\equiv\text{CCF}_3$ , in low yield (197). The main product is the 1:1 adduct  $(\text{CH}_3)_2\text{AsC}(\text{CF}_3)=\text{CHCl}$  (see Section II, A, 9,a), and the propynylarsine probably arises by HCl elimination from the other 1:1 adduct  $(\text{CH}_3)_2\text{AsCH}=\text{CCl}(\text{CF}_3)$  (197).

The formation of As—C bonds from elimination reactions involving arsenic hydrides is almost unknown. Usually the arsine acts as a reducing agent (210). However, it seems that the reactions



take place to a limited extent (204, 210a).

Ylids of arsenic have been obtained by elimination of hydrogen halides from arsonium compounds (211).

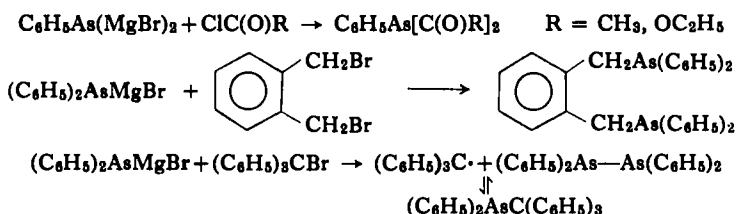


## 11. Reactions Involving Metallic Derivatives of Arsenic

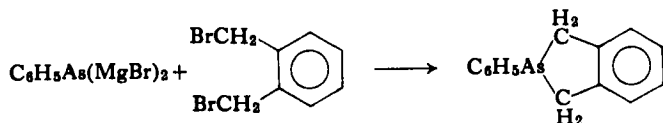
Phenylarsinebis(magnesium bromide) and diphenylarsinemagnesium

<sup>1</sup> It has been suggested that all the aluminum-trichloride-catalyzed reactions with benzene are electrophilic processes (209a).

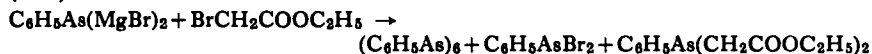
bromide have been known for some time and undergo a variety of coupling reactions such as (210, 212),



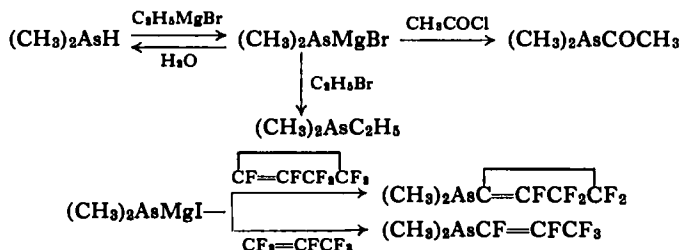
The equilibrium postulated in the last process seems worth further investigation. More recently the "arsenic Grignards" have been used to prepare cyclic arsines (213, 214).



Side reactions can, however, occur, and in some cases become dominant (213).

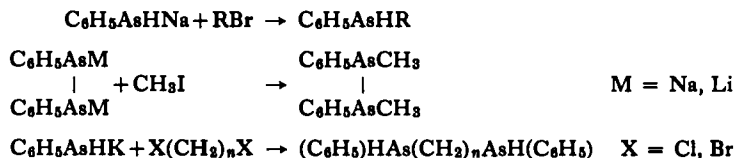


In the aliphatic field only the compound  $(\text{CH}_3)_2\text{AsMgX}$  has been investigated (194, 204). Some typical reactions are as follows:



The novel reaction with fluoroolefins should be capable of extension.

Lithium, sodium, and potassium derivatives of arsenic are also easily prepared and react in much the same manner as do the Grignard derivatives (215-218).



It is worth noting, however, that some complications can arise, as in the following example (163):

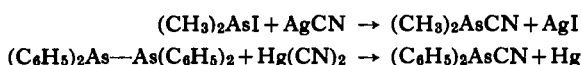


Alkyl iodides also react with metal arsenides on heating. Thus tetramethyldiarsine, trimethylarsine, and tetramethylarsonium iodide are obtained from methyl iodide and sodium arsenide (168). Alkyl iodides and the arsenides of zinc, cadmium, or mercury give mainly compounds of the type  $(\text{R}_4\text{As})_2\text{ZnI}_4$  and  $\text{R}_4\text{AsHgI}_3$  (219, 220). These reactions are related to those described in Section II, A, 2 and probably to those in Section II, A, 5.

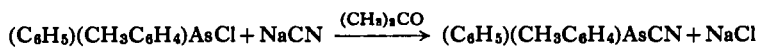
## 12. Miscellaneous Methods

a. *Preparation of Cyanides.* Arsenicals containing cyanide groups directly bonded to arsenic are of interest not only because they contain an As—C bond but also because it has been claimed that cyanides of the type  $\text{R}_2\text{AsCN}$  can be hydrolyzed to carboxylic acid or formamide derivatives such as  $(\text{C}_6\text{H}_5)_2\text{AsCOOH}$  and  $\text{C}_6\text{H}_5\text{AsCONH}_2$  (221).

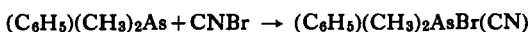
Tervalent cyanides can be obtained from oxides and hydrocyanic acid, from oxides or sulfides and mercuric cyanide, from haloarsines and silver cyanide, and from diarsines and mercuric cyanide (222, 223).



Chloroarsines and alkali metal cyanides also yield cyanoarsines (3, 224).



Pentavalent arsenic cyanides are obtained by adding, for example, cyanogen bromide to arsines of the type  $\text{R}_3\text{As}$  (3).



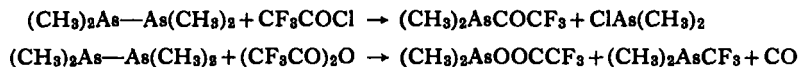
The cyanide is very easily hydrolyzed from derivatives like this yielding hydroxy bromides.

b. *Decarboxylation of Trifluoroacetates.* The following equations illustrate the only successful application of this method (222):

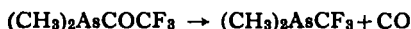


It does not seem to be of great utility (224a).

c. *Preparation and Decarbonylation of Trifluoroacetylarsines.* Tetramethyldiarsine reacts with trifluoroacetyl chloride and trifluoroacetic anhydride at 20° C (210a).

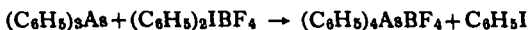


Presumably the trifluoroacetylarsine initially produced in the anhydride cleavage, spontaneously decarbonylates.



Independently this reaction has been found to occur on heating (210a).

d. *Iodonium Salts as Arylating Agents.* A good yield of tetraphenylarsonium tetrafluoroborate was obtained by heating triphenylarsine with diphenyliodonium tetrafluoroborate (225).



e. *Displacement of Amines from Aminoarsines.* The method is illustrated by the one known example but should be capable of considerable extension (197).<sup>2</sup>



f. *Triphenylarsine and Dimethyl Acetylenedicarboxylate.* This reaction was attempted as a means of preparing a pentavalent arsole. However, the product is the arsenylidene oxalacetate (226).



g. *Arsenic Hydrides and Alkoxy Magnesium Compounds.* It is claimed that arsine reacts with derivatives such as  $(\text{CH}_3)_2\text{C}(\text{C}_2\text{H}_5)\text{OMgCl}$  to form arsines such as  $(\text{CH}_3)_2\text{C}(\text{C}_2\text{H}_5)\text{AsH}_2$  (227). The alkoxy magnesium derivative is obtained by treating a carbonyl compound with a Grignard reagent.

h. *High-Energy Particle Synthesis.* When a benzene solution of arsenic trichloride is irradiated with neutrons phenylarsines are produced (228). It has been suggested that useful amounts of compounds of the type

<sup>2</sup> Trifluoropropyne reacts similarly, though slowly, with  $(\text{CH}_3)_2\text{AsSC}_2\text{H}_5$  (197). These results should be compared with the reaction of  $\text{CF}_3\text{C}\equiv\text{CH}$  with  $(\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$  (Section II,A,9,a).

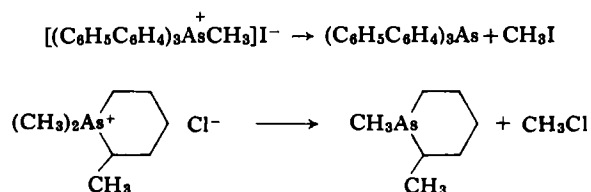
$\text{RAsCl}_2$  are obtained when solutions of arsenic trichloride in hydrocarbons such as cyclohexane are irradiated with 3 MeV electrons (229).

i. *Mycological Methylations*. The investigation of the effect of molds and fungi on arsenic compounds arose because of various poisonings, rightly or wrongly ascribed to *volatile* arsenic compounds liberated from, for example, moldy wallpaper. Many molds have the property of methylating arsenic compounds and Challenger and his co-workers have shown that one of these, *P. brevicaulis*, can methylate a range of compounds. Thus trimethylarsine is obtained from both arsenious oxide and dimethylarsinic acid, and ethylmethyl-*n*-propylarsine from ethyl-*n*-propylarsinic acid (230).

## B. Cleavage of Arsenic–Carbon Bonds

### 1. Thermal Decomposition of Arsonium Compounds

The early failure to resolve arsonium compounds containing alkyl groups attached to arsenic led to the idea that such compounds are easily dissociated (231), and it was found that heating them could reverse the usual method of synthesis and result in the elimination of alkyl halide (59, 232).

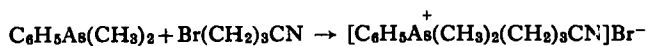


The method has often been used as a means of purifying tertiary arsines since the intermediate arsonium compounds are usually easily prepared and purified.

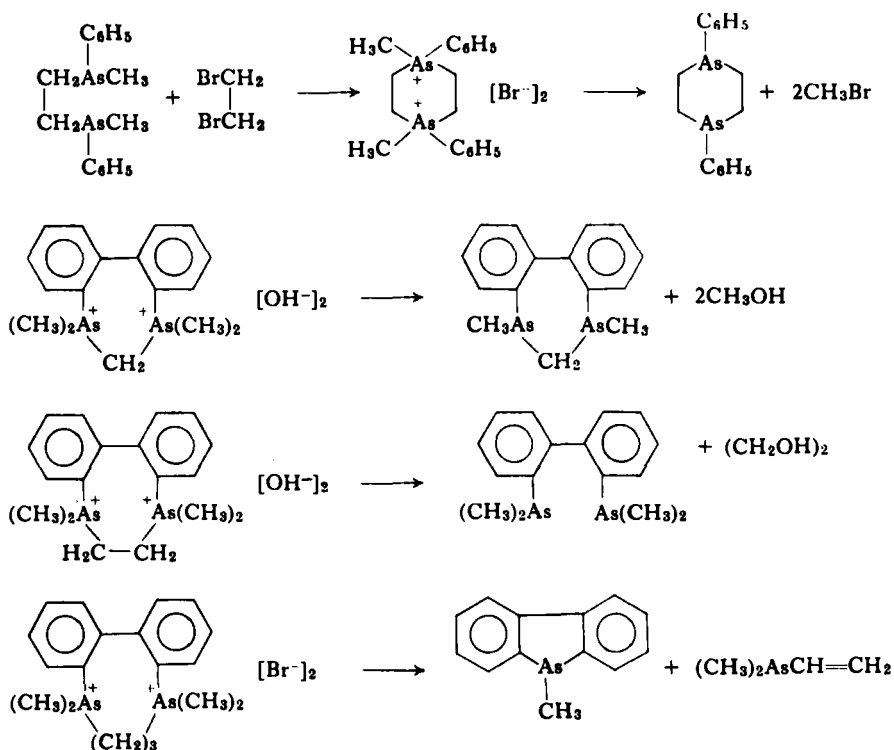
Other arsenicals behave similarly (233).



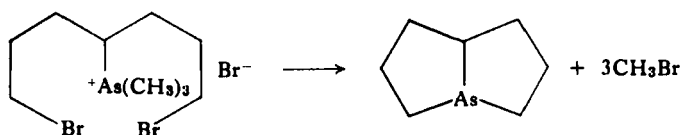
However, it is not always possible to predict which group will be lost (191).



Perhaps the most interesting application of this type of reaction has been the syntheses of heterocyclic arsines (56, 79, 234).



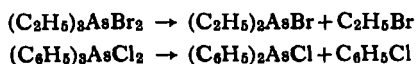
Note especially the ring contraction which occurs in the last example. The structural factors governing this type of thermal decomposition are not clear (79). In the recent synthesis of 1-arsabicyclo[3.3.0]octane the implied route is as follows (235):



Not surprisingly the compound is obtained in low yield.

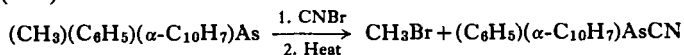
## 2. Cleavage by Halogen

Usually arsines of the type  $\text{R}_3\text{As}$ ,  $\text{R}_2\text{AsX}$ , or  $\text{RAsX}_2$  add halogens to form the pentavalent derivatives  $\text{R}_3\text{AsX}_2$ ,  $\text{R}_2\text{AsX}_3$ , and  $\text{RAsX}_4$ , respectively. On heating, these decompose with loss of  $\text{RX}$  (105):

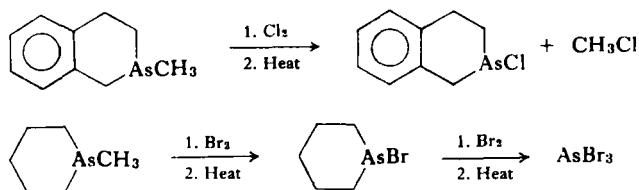




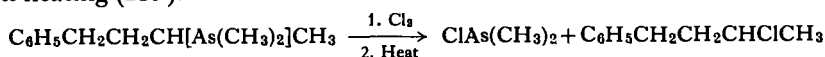
A related reaction, elimination of an alkyl bromide from a pentavalent cyanogen bromide adduct, has been a useful means of preparing cyanoarsines (236).



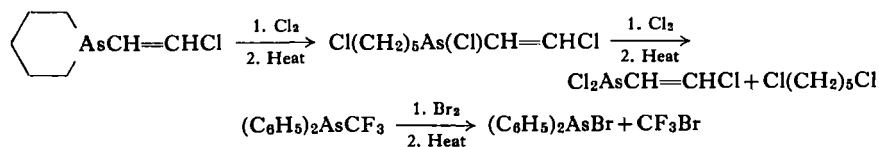
In the heterocyclic field the addition-elimination reaction has been used to replace an alkyl group with a more reactive halogen (63, 237, 238).



However, here again, it is not possible to predict which group will be lost on heating (239).

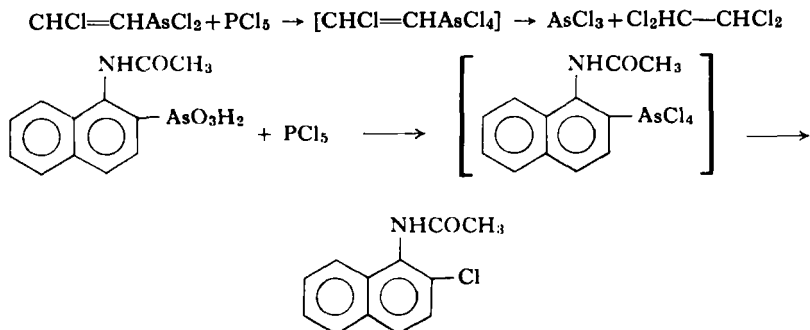


When groups other than methyl are present the situation is even more uncertain (68, 188, 240).

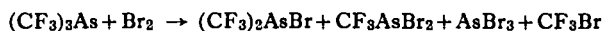


Methyl bromide seems to be lost more easily than bromotrifluoromethane from the dibromide of  $\text{C}_6\text{H}_5\text{As}(\text{CH}_3)\text{CF}_3$  (68).

Phosphorus pentachloride probably cleaves As—C bonds by a related reaction involving formation of pentavalent intermediates (241, 242)

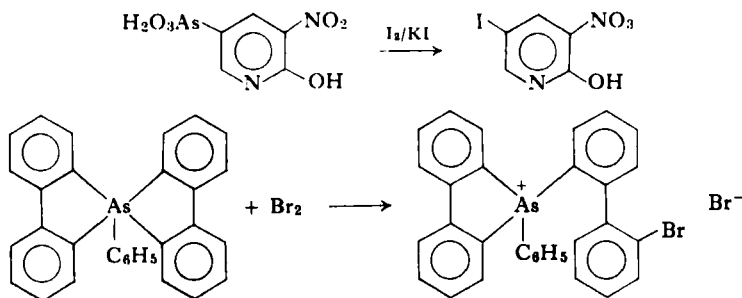


In some cases of cleavage by halogen the intermediate pentavalent compounds are either not formed or are so unstable as to decompose spontaneously. The reaction



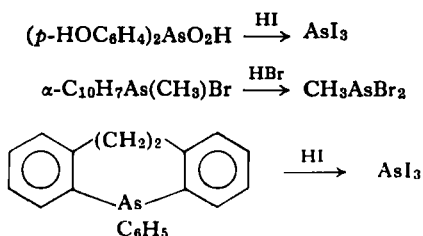
seems to be of this type, even though the corresponding compounds  $(\text{CF}_3)_3\text{AsX}_2$  ( $\text{X} = \text{Cl}, \text{F}$ ) have been isolated (30).

Halogens can also cleave pentavalent arsenicals as in the examples (86, 243)



### 3. Cleavage by Acid

Aryl arsenicals have often been cleaved by acids of the  $\text{HX}$  variety (81, 244, 245).



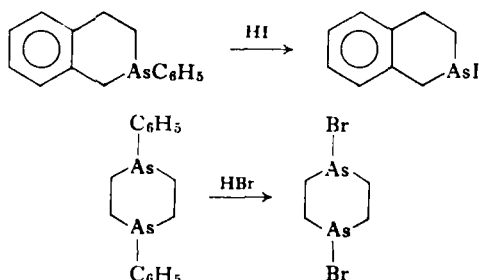
Indeed cleavage of arsonic acids by hydrobromic acid has been suggested as a means of preparing aryl bromides ((246, 247, 248). In the heterocyclic field Gibson and Johnson (249) found that 10-alkyl-5,10-dihydrophenarsazines are decomposed by hydrogen chloride giving alkyldichloroarsines. They suggested this method as a convenient source of this type of compound.



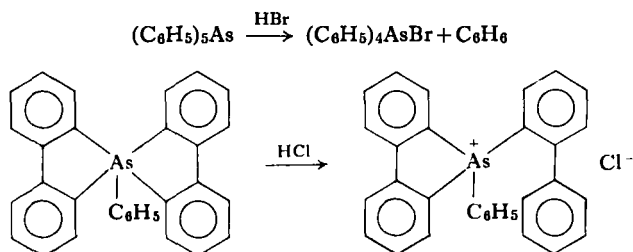
Liquid hydrogen chloride gives better yields (250) and the compound  $\text{CF}_2=\text{CFAsCl}_2$  was recently obtained by this procedure (109). The parent

compound 10-chloro-5,10-dihydrophenarsazine is itself cleaved by hydrogen chloride, yielding arsenic trichloride and diphenylamine (251). The reaction is thus the reverse of the method of synthesis of the 10-chloro compound (7).

The relative stabilities of alkyl and arylarsines to cleavage by HX acids has been exploited to replace phenyl with halogen (56, 81, 213).



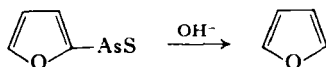
When HI was used instead of HBr in the last example aliphatic As—C bonds were cleaved as well as the aromatic ones (56). The arsenanes are also sensitive to HX (85, 86).



Alkylarsines and arsonium compounds are decomposed to arsenious oxide on heating with sulfuric acid (252).

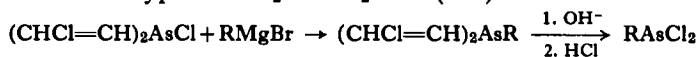
#### 4. Basic Cleavage

Certain derivatives of furan are the only nonaliphatic arsenicals known to be cleaved by base, for example (253),

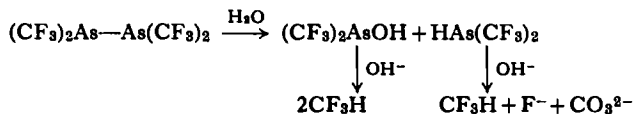


and some furan arsenicals are even unstable to water. Compounds containing unsaturated aliphatic groups such as  $\text{R}_2\text{AsC}\equiv\text{CAsR}_2$  are alkali-sensitive (105) as are the  $\beta$ -chlorovinylarsines. The *trans* derivative  $\text{CHCl}=\text{CHAsCl}_2$

is hydrolyzed quantitatively to acetylene whereas the *cis* compound yields vinyl chloride (182). The rate of hydrolysis of  $(\text{ClCH}=\text{CH})_2\text{AsCl}$  is much slower than that of the corresponding dichloroarsine (254). The following example shows an application of these basic cleavages to the preparation of compounds of the type  $\text{RAsCl}_2$  and  $\text{R}_2\text{AsCl}$  (255):



Nearly all trifluoromethyl arsenicals are hydrolyzed quantitatively by base affording fluoroform. This reaction has been of value in the analysis of these compounds. Exceptions are the compounds  $(\text{CF}_3)_2\text{AsH}$ ,  $\text{CF}_3\text{AsH}_2$ , and  $(\text{CF}_3)_2\text{As}-\text{As}(\text{CF}_3)_2$  which give fluoride and carbonate as well as fluoroform. Hydrolysis of the diarsine is believed to involve hydrolytic fission of the As—As bond (30).



The ease of basic cleavage of the compounds  $\text{R}_n\text{As}(\text{CF}_3)_{3-n}$  ( $n = 0, 1, 2$ ;  $\text{R} = \text{alkyl or } \text{C}_6\text{H}_5$ ) increases as  $n$  decreases (68, 175, 256), and in the alkyl compounds, when  $n = 2$ , the ease of hydrolysis apparently decreases in the order  $\text{CH}_3 > \text{C}_2\text{H}_5 > \text{C}_4\text{H}_9$  (256). These results indicate that hydrolysis involves nucleophilic attack (probably  $\text{S}_{\text{N}}2$ ) by the hydroxide ion on the central arsenic, this atom becoming more positive as the number of electronegative  $\text{CF}_3$  groups is increased (175, 256). The phenyltrifluoromethylarsines are attacked only slowly by aqueous base. However, alcoholic potassium hydroxide is more effective (68).

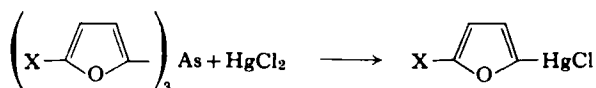
Fluoroform is also produced from trifluoromethyl arsenicals on ammonolysis and aminolysis, the results of ammonolysis studies apparently paralleling those of hydrolysis (68, 256, 257). Sodium methoxide in methanol also liberates fluoroform, although ethanol and methanol react only slowly, if at all, with tris(trifluoromethyl)arsine (256).

Perfluorovinyl dimethylarsine is slowly hydrolyzed by base to trifluoroethylene (70) although reports on the stability of tris(perfluorovinyl)arsine seem to be in conflict (108, 258).

### 5. Cleavage by Mercury Compounds

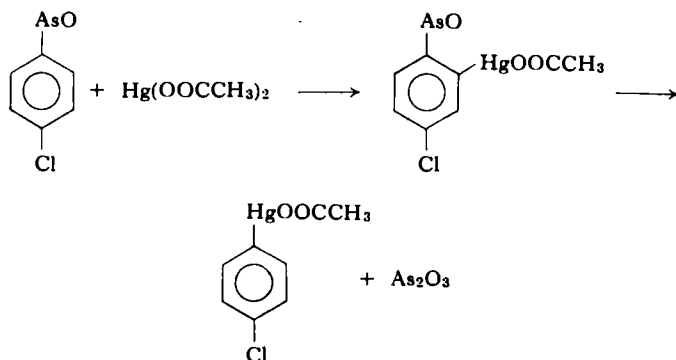
Treatment of phenylarsenious oxide with mercuric oxide under alkaline conditions gives diphenylmercury (259). Dichlorophenylarsine and mercuric chloride do not react in refluxing ethanol (260); Lowe and

Hamilton (253, 261) found that furylarsines can be cleaved under these conditions.

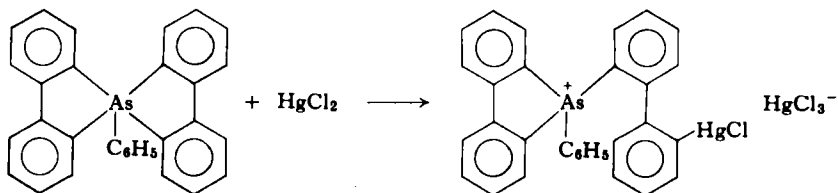


When X = H the reaction goes easily but when X = Cl or Br transfer is more difficult. Bis(2-furyl)arsinic acid does not react, and tris(3-furyl)arsine yields a 1:1 mercuric chloride complex, no cleavage taking place.

Hiratuka (262) has investigated the mercuriation of aryl arsenicals by mercuric acetate. He found that the  $-\text{As}=\text{O}$  or  $-\text{As}(\text{OH})_2$  group facilitates substitution which takes place *para* to the arsenic or *ortho* if the *para* position is blocked. In certain cases, however, the product is unstable, yielding arsenious oxide and an organic mercurial in which the mercury has moved to the position originally occupied by the arsenic-containing group (262, 263).

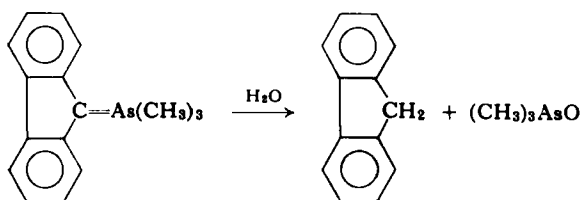


Cleavage of pentaarylsoranes by mercuric chloride occurs readily (86).

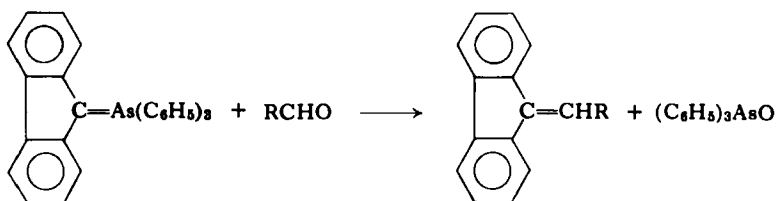


#### 6. Miscellaneous Cleavages of Ylides and Pentaarylsoranes

Wittig and Laib (264) found that fluorenylidene(trimethyl)sorane is decomposed by water, sodium methoxide, or hydroxide, yielding fluorene and trimethylarsine oxide.

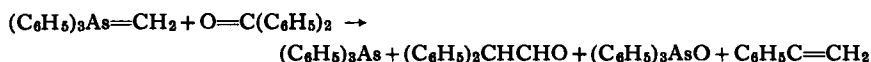


The corresponding derivative of triphenylarsine is cleaved by zinc in hydrochloric acid, or Raney nickel, to give fluorene and triphenylarsine (265). It also takes place in typical Wittig olefin syntheses with aldehydes (211).



$\text{R} = \text{CH}_3, \text{C}_6\text{H}_5, \text{etc.}$

Ketones do not react with this ylid as is the case with the corresponding phosphorus compound. Henry and Wittig (87) report that the ketone, benzophenone, and methylenetriphenylarsorane give mainly diphenylacetaldehyde, only a very low yield of the expected olefin being obtained.

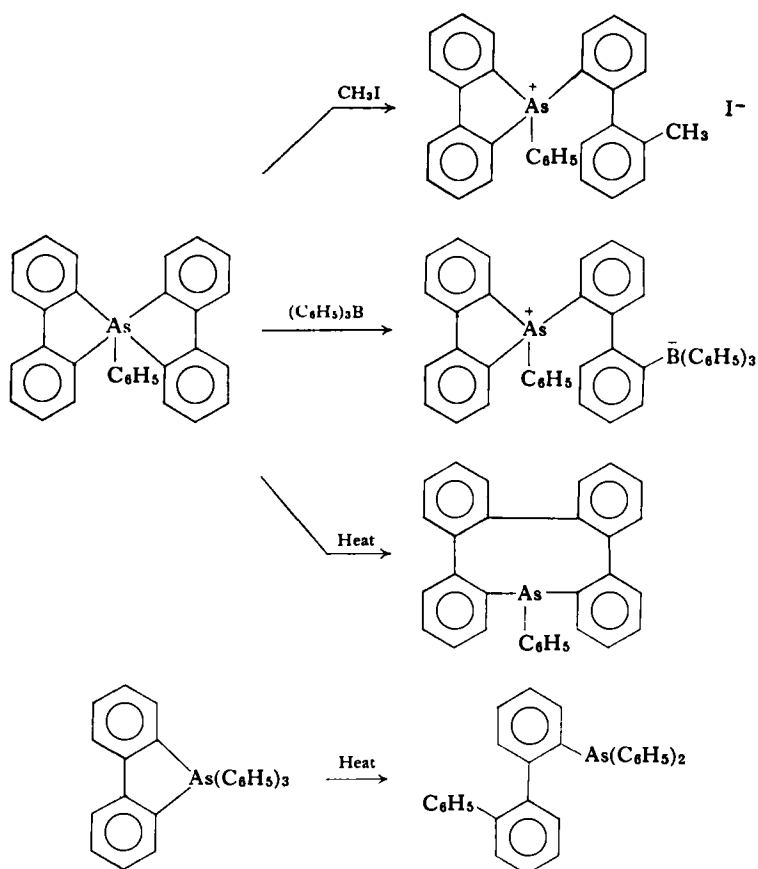


The mechanism of this last reaction has been discussed (266).

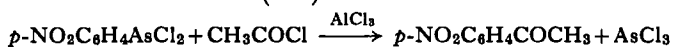
The examples on the opposite page illustrate some novel cleavage reactions found for spiroarsoranes (86).

### 7. Miscellaneous Cleavages of Other Arsenicals

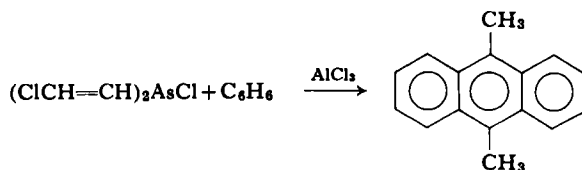
When triphenylarsine in xylene is heated with hydrogen (60 atm) benzene and arsenic are produced (267). Raney nickel cleaves tri-( $\alpha$ -naphthyl)arsine and triphenylarsine yielding binaphthyl and biphenyl respectively (265). Nickel-aluminum alloy in aqueous alkali gives aniline from arsanilic acid (268), and sodium amide in boiling piperidine cleaves benzenearsonic acid (269). Phenyl groups are also lost from triphenylarsine when this is irradiated with thermal neutrons (270).



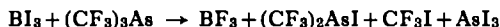
Arylarsines on refluxing with acyl chlorides in the presence of aluminum trichloride form chloroarsines (271).



This reaction has been suggested as a means of locating the point of attachment of the arsenic, since the RCO group of the acyl halide takes its place (272). When  $\beta$ -chlorovinylarsines are refluxed in benzene with aluminum trichloride, 9,10-dimethylantracene is produced (273).

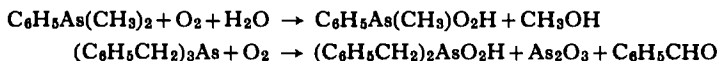


Trifluoromethyl groups are lost from tris(trifluoromethyl)arsine on heating with aluminum trichloride, aluminum triiodide, or boron triiodide (130).



When tris(trifluoromethyl)arsine and nitric oxide are heated or irradiated, trifluoronitrosomethane is obtained in small amounts (130, 274). The same compound is also produced when the arsine is heated with nitrosyl chloride (274).

Claims have been made that oxidation of alkylarsines by air leads to alkylarsenic oxides of the type  $(\text{CH}_3)_3\text{AsO}$  (3). In a number of cases it has since been found that this oxidation is accompanied by cleavage of an alkyl group (275, 276).



Zingaro and Meyers (277) have recently suggested that lack of success in preparing trialkylarsenic oxides by direct oxidation of arsines indicates the necessity of a careful reinvestigation of the claims for the existence of these compounds. However, oxidation with hydrogen peroxide does seem to give the required products (278).

Arsenic-carbon bonds are also cleaved by alkali metals (Section II, C, 2) and a number of other reactions such as disproportionation and thermal decomposition which involve rupture of these bonds are described in other Sections of this review.

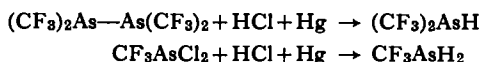
### C. Arsenicals Having Arsenic Atoms Sigma-Bonded to Other Elements: Preparation of Compounds with C—As—X Units

#### 1. *X = Hydrogen*

The original method for preparing compounds of the type  $\text{R}_2\text{AsH}$  and  $\text{RAsH}_2$  was to reduce the appropriate arsonic or arsinic acid, oxide, or halide with amalgamated zinc and hydrochloric acid (3) and it is still good for obtaining the more volatile derivatives. Wigren (279) obtained unsymmetrical dialkylarsines in this way, and the trifluoromethylarsines  $(\text{CF}_3)_2\text{AsH}$  and  $\text{CF}_3\text{AsH}_2$  were similarly obtained from the corresponding iodides (30). However, the trifluoromethylarsines are more conveniently



prepared by reduction of the appropriate compounds with mercury in the presence of dry hydrogen chloride (130, 280) (cf. Section II, A, 5).

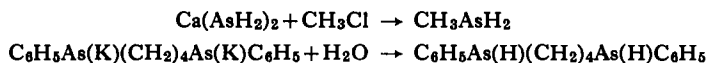


Lithium aluminum hydride reduces dialkylchloroarsines in good yield (97, 280a), but lithium borohydride is superior for reducing chlorophenylarsines (281). The borohydride has also been used to obtain the arsenic homologs of piperidine and pyrrolidine (282).

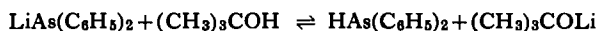


Attempts to prepare compounds of the type  $(\text{C}_6\text{H}_5)_n\text{AsH}_{5-n}$ , ( $n = 1-4$ ) by reducing the compounds  $(\text{C}_6\text{H}_5)_n\text{AsCl}_{5-n}$  with either lithium borohydride or aluminum hydride were unsuccessful. The only products isolated were the trivalent compounds  $(\text{C}_6\text{H}_5)_n\text{AsH}_{3-n}$  (283).

Triethyltin hydride reduces chlorodimethylarsine quantitatively to dimethylarsine (283a). Substituted arsenic hydrides are also produced by coupling and by hydrolysis reactions involving metal derivatives of arsenic hydrides (163, 284).



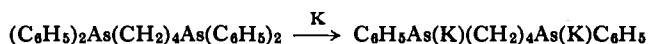
Metal-hydrogen exchange reactions also afford arsines, as in the example,



The As—H acidities of a number of arsines have been determined by studies of this and related equilibria (285).

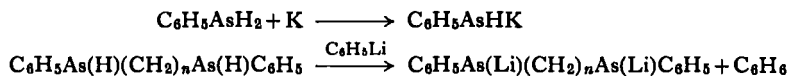
## 2. *X = Group I Element*

Lithium-, sodium-, and potassium-arsenic derivatives are known. Thus triphenylarsine is cleaved by sodium in liquid ammonia (286), by potassium in dioxane (163), and by lithium in tetrahydrofuran (287) to give compounds  $(\text{C}_6\text{H}_5)_2\text{AsM}$  ( $\text{M} = \text{Li}, \text{Na}, \text{K}$ ). Other phenylarsines are similarly cleaved (163).

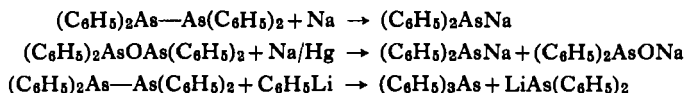


However, potassium in dioxane does not react with dialkylarylsarsines or trialkylarsines (287a).

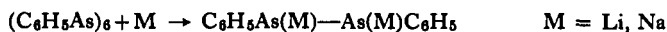
Arsenic hydrides are useful sources of this type of compound, reacting with sodium in liquid ammonia (215) or tetrahydrofuran (288), with potassium in dioxane or benzene (218), and with lithium, lithium alkyls and aryls, lithium alkoxides, lithium amides in various solvents (218, 280a, 287a). Derivatives such as  $(C_6H_5)_2AsK$  and  $C_6H_5AsHK$  can be isolated from dioxane as solvated crystals (163, 218).



Compounds with As—As and As—O bonds are cleaved by alkali metals (64), and the As—As bond also reacts with phenyllithium (91c).



Arsenobenzene and lithium or sodium give the diarsine derivative (216, 217).

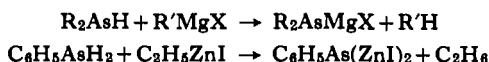


With excess sodium the fully cleaved product,  $C_6H_5AsNa_2$ , is obtained. Reesor and Wright (216) suggest that the diarsine derivative can be made from the disodio derivative by treating the latter with arsenobenzene.



### 3. *X = Group II Derivative*

This type of compound is prepared by reacting arsenic hydrides with Grignard reagents, or in one case with ethylzinc iodide (212).



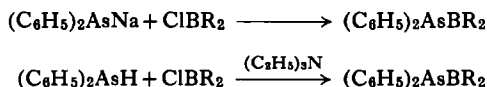
$R'$  can be alkyl or aryl and  $R$  has *usually* been aryl (212, 214), though more recently the dimethyl compounds  $(CH_3)_2AsMgX$  ( $X = Br, I$ ) have been prepared (194, 204). Trialkyl- and triarylarisines react with alkylmercury halides affording salts containing ions such as  $[CH_3HgAs(C_2H_5)_3]^+$  (288a).

### 4. *X = Group III Derivative*

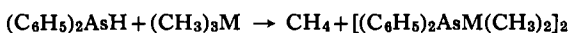
The first arsenical of this type was prepared by Stone and Burg (284), viz.,



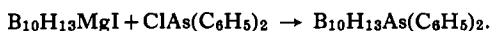
The trimer,  $n = 3$ , which is almost certainly cyclic, was the main product. The tetramer and a higher polymer were also obtained. The complex  $(\text{CH}_3)_2\text{AsBH}_3$  decomposes at room temperature to give a polymer. The related boron compounds  $(\text{C}_6\text{H}_5)_2\text{AsBR}_2$  ( $\text{R} = \text{aryl}$ ), which appear to be monomeric in solution, have been prepared by other methods (288).



Diphenylarsine and the compounds  $(\text{CH}_3)_3\text{M}$  ( $\text{M} = \text{Al}, \text{Ga}, \text{In}$ ) eliminate methane spontaneously (289).

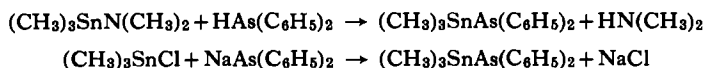


The Grignard reagent formed from decaborane-14 couples with chlorodiphenylarsine as follows (290):

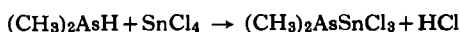


### 5. $X = \text{Group IV Derivative}$

Very few arsenicals of this type are known. Maier (291) has found that triphenylsilyl lithium couples with dibromomethylarsine forming  $\text{CH}_3\text{As}[\text{Si}(\text{C}_6\text{H}_5)_3]_2$ . Dimethylaminotrimethyltin and diphenylarsine give a nearly quantitative yield of diphenyl(trimethylstannyl)arsine (292). Similar compounds are obtained from trialkyltin halides and the sodium derivative of diphenylarsine (178a).



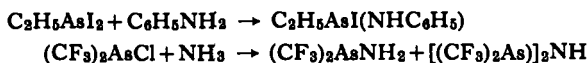
A rather unusual coupling reaction is reported to take place between dimethylarsine and tin tetrachloride (293).



### 6. $X = \text{Group V Derivative}$

a. *Nitrogen*. Dichlorophenylarsine and dry ammonia in benzene solution react exothermically to give  $(\text{C}_6\text{H}_5\text{AsNH})_n$ , which is probably a tetramer. The analogous methyl compound  $[(\text{CH}_3\text{AsNH})_n]$  is similarly prepared

(294). This reaction of haloarsines with amines has since been extended (257, 295, 296).

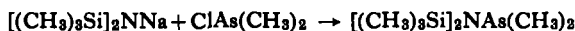


It is worth noting that arsenic trichloride and diphenylamine produce phenarsazine chloride (Section II, A, 10) in which arsenic is attached to carbon atoms in the aromatic rings rather than to the nitrogen. Thus the formation of As—N bonds by this method appears to be a function of the base strength of the amine.

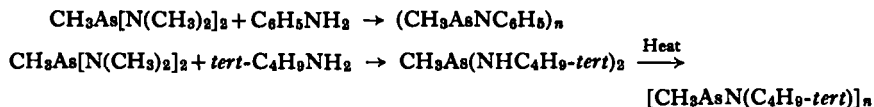
Aminoarsines are intermediate products in the ammonolysis and aminolysis of trifluoromethylarsines (257). (See Section II, B, 4)



They are also obtained from the reaction of metal amides with haloarsines (91b, 297)



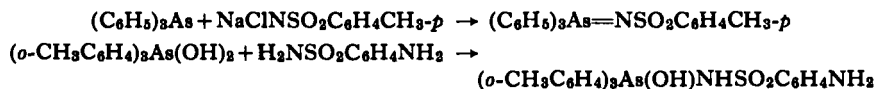
Alkylamino groups on arsenic can be replaced by other homologs (298).



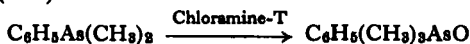
The last product is apparently the diazodiarsacyclobutane ( $n = 2$ ). Another cyclic arsenical has been prepared (299) using a method developed for preparing the corresponding phosphonitrilic compounds.



The reaction of arsines with chloramine-T and related compounds gives rise to arsinimines (86, 300) though these are usually isolated as the hydroxy sulfonamides (300, 301, 302). The hydrated compounds can also be prepared from the tertiary arsine oxide, or dihydroxide, and the appropriate amine.

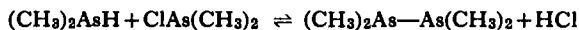


In some cases the arsinimine, or its hydrate, is unstable, decomposing to the arsine oxide (302).



The parent compound,  $(\text{C}_6\text{H}_5)_3\text{As}=\text{NH}$ , has been prepared (303).

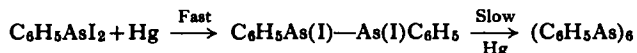
b. *Arsenic*. As indicated in the Introduction, tetramethyldiarsine was one of the first organoarsenic compounds to be prepared. This diarsine can be obtained by Cadet's method (Section II, A, 1), by reducing dimethylarsinic acid with hypophosphorous acid or the compounds  $(\text{CH}_3)_2\text{AsX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{S}_4$ ) with mercury or zinc, or by the union of chlorodimethylarsine and dimethylarsine (3, 293).



This last reaction is reversible (71). Tetrakis(trifluoromethyl)diarsine and tetraphenyldiarsine are formed by analogous reactions (71, 304), and it also appears that the only known unsymmetrical diarsine,  $(\text{CF}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$ , can be prepared from bis(trifluoromethyl)arsine and chlorodimethylarsine. However, the reaction of chlorobis(trifluoromethyl)arsine with dimethylarsine gives rise to many products (71).

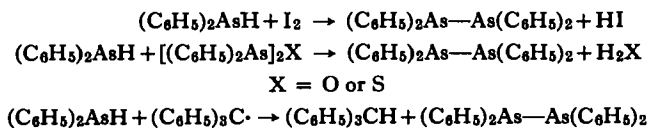
Tetrakis(trifluoromethyl)diarsine can also be obtained by reduction of the compounds  $(\text{CF}_3)_2\text{AsX}$  ( $\text{X} = \text{Cl}, \text{I}, \text{S}_4$ ) with mercury at  $20^\circ \text{C}$  (30, 71, 178). Tetraaryldiarsines are available from similar reactions (305), although the most convenient method of preparing these compounds is by reducing the corresponding oxides or hydroxides with hypophosphorous acid (3).

The diarsine,  $\text{C}_6\text{H}_5\text{As}(\text{I})-\text{As}(\text{I})\text{C}_6\text{H}_5$ , which is usually prepared by reduction of diiodophenylarsine with phosphorous acid, is also the major product of the reduction of the same diiodide with mercury. A much slower reduction to arsenobenzene also takes place (306).



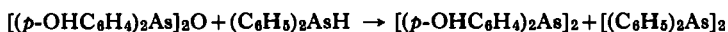
Compounds of the type  $\text{C}_6\text{H}_5\text{As}(\text{Br})-\text{As}(\text{Br})\text{C}_6\text{H}_5$  are also known but not the chloro analogs. The diiododiarsine also results from phenylarsenious oxide and diiodophenylarsine, from arsenobenzene and iodine, and from phenylarsine and iodine (306). However, if excess iodine is used in this last reaction diiodophenylarsine is produced quantitatively (307).

Blicke and Powers (307) found that tetraphenyldiarsine is produced by a number of other reactions.

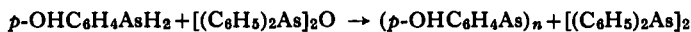


The reaction of hydride with oxide has been studied as a means of preparing

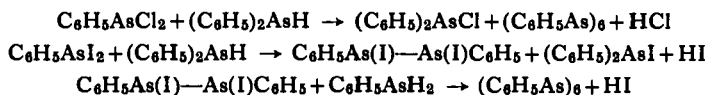
unsymmetrical diarsines  $R_2As-AsR_2'$  but without success, the products being the two symmetrical diarsines (308, 309).



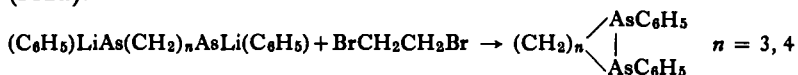
A similar reaction occurs with bis(diphenylarsenic) oxide and primary arylarsines (309).



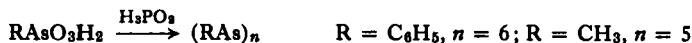
Some work reported (310) claiming the preparation of compounds like  $(C_6H_5)_2As-As(Cl)C_6H_5$  [from  $C_6H_5AsCl_2$  and  $C_6H_5AsH_2$ ],  $(C_6H_5)_2As-As(C_6H_5)-As(C_6H_5)_2$  [from  $C_6H_5AsI_2$  and  $2(C_6H_5)_2AsH$ ], and  $C_6H_5As-As(C_6H_5)-As(C_6H_5)_2$  [from  $C_6H_5As(I)-As(I)C_6H_5$  and  $C_6H_5AsH_2$ ] has since been found to be incorrect (304, 311, 312). It seems that these reactions are best represented as follows:



Mention has been made above (Section II, A, 11) that tetraphenyldiarsine is obtained from ethylene dibromide and  $(C_6H_5)_2AsK$ , and recently this type of reaction has been extended to prepare a diarsacyclopentane and -hexane (312a).



Arsenomethane and arsenobenzenes are usually prepared by reduction of the corresponding acid (3).



These arseno compounds are cyclic (Section III, A). Other reducing agents such as phosphorous acid, or stannous chloride in hydrochloric acid, can be used. Arsenobenzene can be obtained from dichlorophenylarsine and sodium, and arseno-*p*-toluene is similarly prepared (61). Unsymmetrical arsenobenzenes have been made by coupling arylarsines ( $RA_sH_2$ ) with the oxides ( $R'AsO$ ) or halides ( $R'AsCl_2$ ) or by reducing a mixture of arsonic acids. One example of a mixed alkylarylarsenobenzene is known (3).

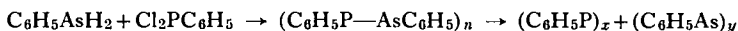


A recent investigation indicates that these mixed arsenobenzenes have a real existence (313). However, in view of the structure of arsenobenzene itself

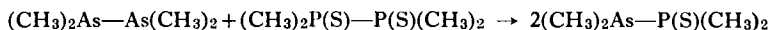
(Section III, A), they are probably made up of a random arrangement of AsR and AsR' groups.

Mention should also be made in this section of the so-called arseno-polysulfides, "RAs(S)=As(S)R," obtained from arsine oxides by treatment with a sulfurizing agent in acid medium. Mixed compounds such as  $\text{CH}_3\text{As}(\text{S})=\text{As}(\text{S})\text{C}_2\text{H}_5$  are also claimed (314). Arylarsino arsenides  $[(\text{RAs})_m\text{As}_n]$  have also been claimed to be produced by treating  $\text{RAsH}_2$  with  $\text{As}_2\text{O}_3$  or  $\text{AsCl}_3$  (315).

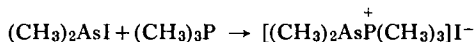
c. *Phosphorus, Antimony, and Bismuth.* Dichlorophenylphosphine and phenylarsine are reported to combine to give phosphoarsenobenzene, which decomposes into phosphobenzene and arsenobenzene (316).



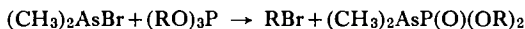
A reaction which is formally the reverse of this decomposition occurs when tetramethyldiarsine and tetramethyldiphosphine disulfide are heated (316a).



Compounds with As—P bonds are also formed from haloarsines and tertiary phosphines (317).

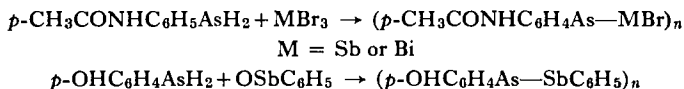


Similar compounds are reported from the related reaction with trialkyl phosphites (318).



However, since the analogously obtained " $\text{R}_3\text{SnP}(\text{O})(\text{OR}')_2$ " compounds have been shown to contain Sn—O—P units (319), the arsenic compounds need confirmation.

Arsenicals with As—Sb and As—Si bonds have been obtained from reactions of the sort used for preparing arseno compounds (3, 320).

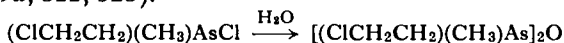


Here again more structural information is needed.

## 7. X = Group VI Derivative

a. *Oxygen.* Many of the methods described in Section II, A, afford arsenicals containing C—As—O units. For example, the Meyer and Bart reactions produce acids of the type  $\text{RAsO}_3\text{H}_2$ , and oxides such as  $(\text{R}_2\text{As})_2\text{O}$  are obtained by Cadet's method and from the reaction of Grignard reagents

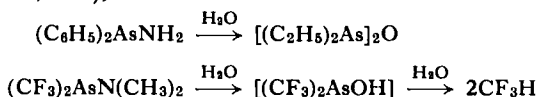
with arsenious oxide. Many of the other synthetic methods result in compounds such as  $\text{RAsX}_2$  and  $\text{R}_2\text{AsX}$ , which are readily hydrolyzed by aqueous sodium hydroxide or carbonate to give the oxides  $\text{RAsO}$  and  $(\text{R}_2\text{As})_2\text{O}$ , respectively (3). In a few cases base hydrolysis gives rise to hydroxides of the type  $\text{R}_2\text{AsOH}$ , especially when R is a nitro-substituted aryl group (3, 321). A certain amount of hydrolysis of haloarsines by water alone takes place (51, 209a, 322, 323).



Base hydrolysis of this chloroethylarsine liberates ethylene (51) (cf. Section II, B, 4).

Hydrolyses of halo arsenicals  $\text{R}_n\text{AsX}_{5-n}$  [ $n = 1-3$ ] is also easy and in most cases intermediate products such as the hydroxychlorides  $\text{R}_3\text{As}(\text{OH})\text{Cl}$  can be isolated (3). Water alone is usually sufficient to remove one of the halogens but removal of the remaining ones often requires more drastic conditions.

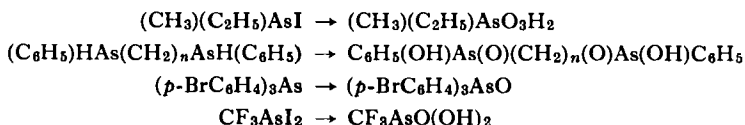
Other arsenicals which are hydrolyzed to the corresponding oxides by water include compounds containing amino, alkoxy, and mercapto groups, for example (257, 294),



It is worth noting that whereas alkoxides of the type  $\text{RAs}(\text{OR}')_2$  are hydrolyzed irreversibly, the corresponding sulfur compounds are hydrolyzed reversibly (323). Simple thioethers are also hydrolyzed more readily than are the cyclic derivatives  $\text{RAsSR}'\text{S}$ .

Oxides and hydroxides are also produced by reduction of arsonic and arsinic acids, sulfur dioxide being usually used, though other reducing agents such as phosphorus trichloride and phenylhydrazine are effective (3, 51, 324, 325, 325a).

Oxidation also leads to formation of new As—O bonds, the most versatile reagent being hydrogen peroxide, although permanganate and nitric acid have had occasional use. The following oxidations have all been accomplished with hydrogen peroxide (173, 218, 279, 326):



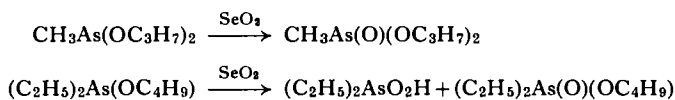


Triphenylarsenic oxide is formed in oxygen transfer reactions involving triphenylarsine and certain oxygen-containing compounds such as 1-pyrroline-1-oxides and thiolsulfinates (327, 328).



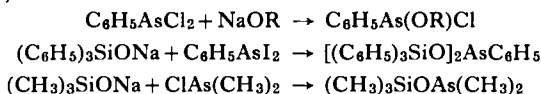
Atmospheric oxidation of arsenic hydrides and diarsines, usually violent, gives a mixture of products which can include the trivalent oxide and pentavalent acid (3, 329). Under controlled conditions tetraaryldiarsines take up one mole of oxygen per mole of diarsine (329). Atmospheric oxidation of other arsenic compounds, apart from those rich in alkyl groups with a small number of carbon atoms, is usually very much slower. [See also Section II, B,7].

Selenium dioxide oxidizes triphenylarsine to the arsenic oxide, the selenide  $(\text{C}_6\text{H}_5)_3\text{AsSe}$  also being produced (330). The dioxide has also been used to oxidize esters of the type  $\text{RAs}(\text{OR}')_2$  and  $\text{R}_2\text{As}(\text{OR}')$  (331, 332).

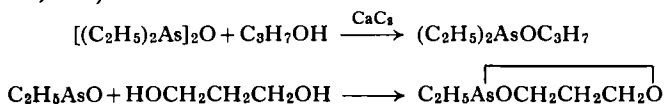


The first example goes in good yield but in the second the yield is low. Note also that loss of an  $\text{OR}'$  group can occur. Mercuric oxide has been used in place of selenium dioxide (332).

The reaction of haloarsines with sodium alkoxides or aryloxides has long been known as a source of arsines containing  $\text{As}-\text{OR}$  groups (3), and more recently such reactions have been used to prepare a variety of derivatives (333, 334, 335).

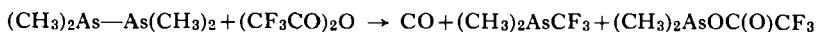
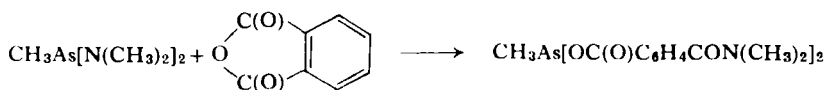


However, Kamai and co-workers, who have done a great deal of work in this area, have found the reaction of this type can be complicated by incompleteness and undesired side reactions (336). They prefer to obtain their products, especially alkoxides, by treating alcohols with arsenic oxides, usually in the presence of a dehydrating agent such as calcium carbide or anhydrous copper sulfate (336, 337).

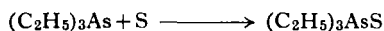
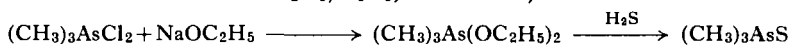
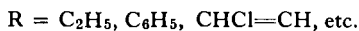
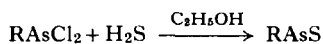




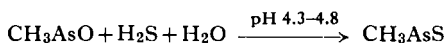
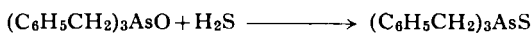
Cleavage of As—As and As—N bonds can also give rise to derivatives of this sort (210a, 346).



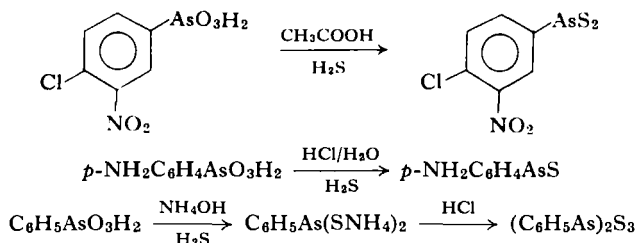
b. *Sulfur and Selenium.* Arsenic sulfides can be prepared by methods analogous to those used for oxides. Thus compounds of the type  $(\text{R}_2\text{As})_2\text{S}$  and  $\text{RAsS}$  are prepared by the action of hydrogen sulfide, or sodium sulfide, on haloarsines (347), and compounds such as  $\text{R}_3\text{AsS}$  from hydrogen sulfide and  $\text{R}_3\text{AsX}_2$  or by direct interaction of a tertiary arsine with elemental sulfur (348, 349).



Hydrogen sulfide also reacts with arsenic oxides to produce the corresponding sulfide (350, 351).

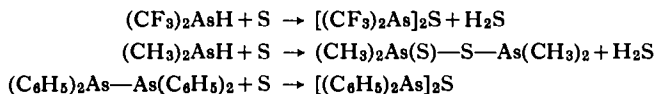


Sulfides are also obtained by reducing arsonic or arsenic acids with hydrogen sulfide, the product depending on the conditions. Thus, in aqueous solution dimethylarsinic acid is reduced to the sulfide  $[(\text{CH}_3)_2\text{As}]_2\text{S}$ , whereas from alcohol the disulfide  $(\text{CH}_3)_2\text{As}(\text{S})\text{—S—As}(\text{CH}_3)_2$  is obtained (352, 353). Arylarsonic acids can react with hydrogen sulfide to give three types of product viz. (354, 355, 356),



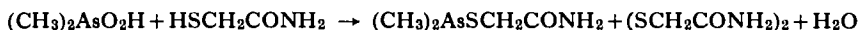
Sulfides of all of the above-mentioned types are obtained by heating arsenicals with carbon disulfide (3, 357).

Whereas oxygen reacts with compounds containing As—H and As—As bonds in rather an uncontrolled manner, the action of sulfur is milder and the method has synthetic use, for example (178, 358),

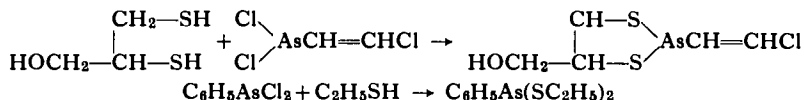


Other less common methods of obtaining sulfides include treatment of iodoarsines with silver sulfide (178), phenylarsine with thionyl chloride (359), and arsenic hydrides with liquid sulfur dioxide (293). Triarylsulfides and disulfur dichloride yield adducts formulated as  $\text{R}_3\text{As}(\text{SSCl})\text{Cl}$  which, on treatment with hydrogen sulfide, give the arsenic sulfide  $\text{R}_3\text{AsS}$  (3).

Mercapto derivatives were first prepared by reducing arylarsonic acids with the appropriate mercaptan, for example (360),

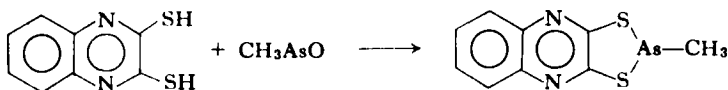


Another well-known method involves treating a chloroarsine with a mercaptan (361, 362).

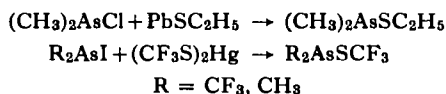


The 2,3-dimercaptopropanol because of this reaction became known as British Anti-Lewisite (BAL). The biological importance of this type of reaction has been discussed by Waters and Stock (363).

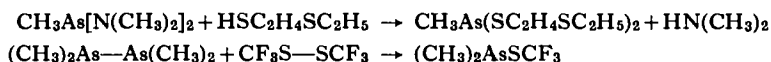
Thioesters are also produced from arsine oxides and mercaptans (364, 365),



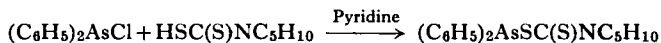
and from mercaptides and haloarsines (178, 256, 366, 367).



Other methods used include displacement of an amine from an aminoarsine by a mercaptan and the cleavage of a diarsine by a disulfide (338, 367).

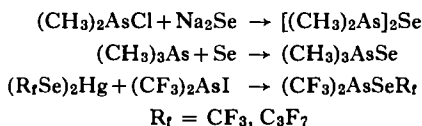


Formation of arsenic-containing derivatives of dithiocarbamic acid has been suggested as a means of identifying arsenicals of the type  $\text{RAsX}_2$  and  $\text{R}_2\text{AsX}$  (368).



Recently the preparation of this type of derivative has been extended because of possible use in agriculture (369, 370).

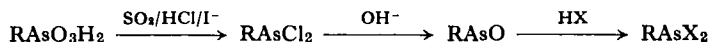
Selenium-containing arsenicals are not well known. The following equations show that the methods of preparation so far available parallel those used for the sulfur-containing analogs (352, 366, 371).



#### 8. $X = \text{Halogen}$

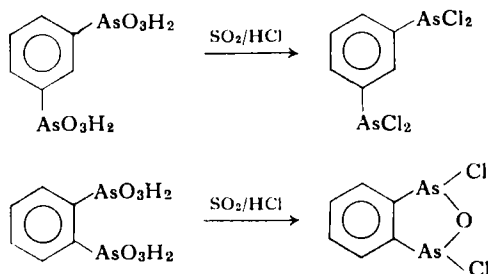
Many of the methods described in Section II, A for the preparation of compounds with As—C bonds also result in compounds with arsenic-halogen bonds. These bonds are also produced by disproportionation and cleavage reactions (Section II, B). Previously mentioned reactions will not be discussed further in this section.

Haloarsines are usually obtained by reducing an arsonic or arsinic acid in the presence of a hydrogen halide. The process may be thought of as involving reduction to the corresponding oxide followed by reaction of the oxide with the acid to give the haloarsine. However, Kappelmeier suggests that in the acid solution the haloarsine is produced by reduction of intermediates such as  $(\text{C}_6\text{H}_5)_2\text{As}(\text{OH})_2\text{Cl}$  (372). The reducing agent most commonly employed is sulfur dioxide although others such as hypophosphorous acid have been used. Reduction is catalyzed by iodide ion, and is usually carried out in hydrochloric acid solution thus giving chloro compounds. These can be purified or converted to other derivatives by hydrolyzing them to the corresponding oxides, purifying the oxides, and then reacting the oxides with the appropriate hydrogen halide (373).



This method is particularly suitable for obtaining haloarsines from the crude reaction mixture obtained from the Meyer and Bart syntheses of

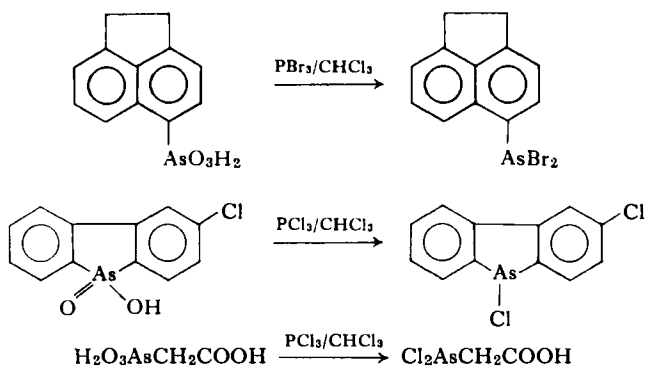
arsonic and arsinic acids (44). The completely chlorinated product is not, however, always obtained (324, 374): e.g.,



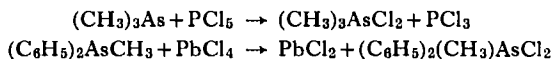
The oxychloride produced in the second reaction seems to be particularly stable and requires more drastic conditions to rupture the As—O bonds and give the tetrachloro compound (375).

Reduction of arsenic acids with sulfur dioxide in the presence of the other acids HX (X = Br, I) gives the expected bromo and iodoarsines (3, 49), and in some cases hydrogen iodide is a sufficiently strong reducing agent to produce the iodoarsine by itself (321). These reductions can also be carried out in acetic acid or sulfuric acid solutions (309, 376).

Phosphorus trihalides have also been used to reduce the acids and recent applications include the following (377, 378):

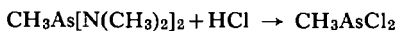


The reverse reaction, oxidation, occurs when a tertiary arsine is treated with phosphorus pentachloride or lead tetrachloride (379, 380).

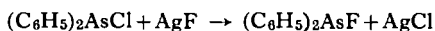
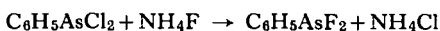


Lead(IV) chloride has been recommended as a reagent for adding chlorine to arsines.

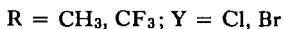
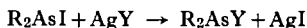
As mentioned above, oxides readily react with hydrogen halides to give haloarsines (3), and aminoarsines also do this (97, 296).



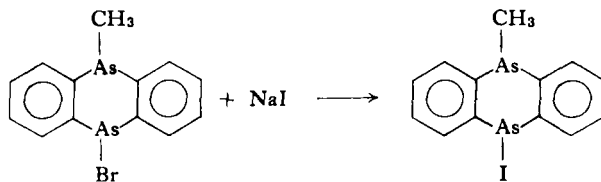
However, only a few reports are available describing the preparation of fluoroarsines by reactions of this type (245, 352), and it seems that the best way of obtaining these derivatives is by treating chloroarsines with either ammonium fluoride or silver fluoride (381, 382).



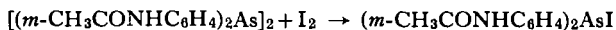
Reactions similar to the last, using mercuric or silver halides, have been used to prepare other haloarsines from the iodo derivatives (29, 222).



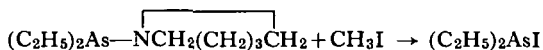
This method is also used to obtain pseudohalogen derivatives. Iodoarsines are available from their chloro and bromo analogs by reacting these with sodium iodide in acetone (3), for example (383),



Haloarsines are obtained from a number of cleavage reactions of compounds with As—As bonds. Halogens react very readily with diarsines, a result which has been of value in characterizing these compounds (308).

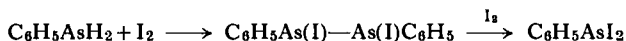


Cyanogen bromide and tetraphenyldiarsine give bromodiphenylarsine in good yield and the same diarsine reacts with a number of inorganic halides such as arsenic trichloride or disulfur dichloride yielding the halodiphenylarsine (358). As described in Section II, A, alkyl halides cleave As—As bonds giving alkylarsines and haloarsines. In a similar fashion methyl iodide cleaves the As—N bond to give iodoarsines (97).

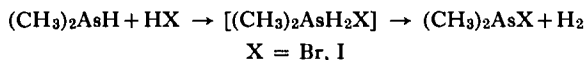


Acyl halides interact with esters of arsenious acids yielding haloarsines (384).

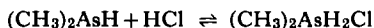
A number of reactions of arsenic hydrides with halogens, hydrogen halides, and inorganic halides also give rise to haloarsines (3), for example (307),



Dichloroethylarsine is produced from ethylarsine by reaction with the chlorides of mercury, tin, phosphorus, arsenic, or antimony (58). Dimethylarsine reacts with hydrogen iodide or bromide to give the halodimethylarsine (293).

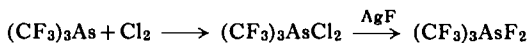


This last reaction is believed to proceed through an arsonium intermediate, as indicated. Hydrogen chloride has been found to react differently with the arsine, giving rise to an arsonium compound which decomposes reversibly (71).



Arsenicals of the types  $\text{R}_3\text{AsX}_2$ ,  $\text{R}_2\text{AsX}_3$ , and  $\text{RAsX}_4$  are usually prepared by direct addition of the appropriate halogen to the corresponding As(III) derivative. Thus Michaelis found that triphenylarsine in chloroform solution readily reacts with chlorine and bromine. Iodine, however, gives the tetraiodide  $(\text{C}_6\text{H}_5)_3\text{AsI}_4$  (385). The diiodide can be obtained from its constituents in petroleum ether (169). There are very few examples known of compounds of the type  $\text{R}_2\text{AsX}_3$  and  $\text{RAsX}_4$ .

Pentavalent fluorides such as  $(\text{C}_6\text{H}_5)_3\text{AsF}_2$  and  $\text{C}_6\text{H}_5\text{AsF}_4$  can be obtained by fluorinating triphenylarsine and phenylarsonic acid, respectively, with sulfur tetrafluoride (386). The corresponding trifluoromethyl compound,  $(\text{CF}_3)_3\text{AsF}_2$ , cannot be prepared by fluorinating tris(trifluoromethyl)arsine with either fluorine or cobalt trifluoride, but it is available by the following procedure (30):



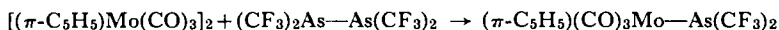
Chlorination of tris(trifluoromethyl)arsine gives the dichloro compound,  $(\text{CF}_3)_3\text{AsCl}_2$ , but under certain conditions cleavage can occur to yield the compound  $(\text{CF}_3)_2\text{AsCl}_3$  (30).

Zingaro and Meyers have obtained compounds of the type  $\text{R}_3\text{AsI}_4$  ( $\text{R} = \text{CH}_3$ ,  $\text{C}_2\text{H}_5$ , or  $\text{C}_6\text{H}_5$ ) by reacting the corresponding sulfide with iodine (277).

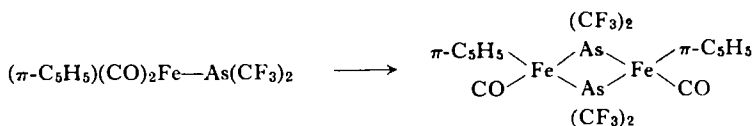


### 9. $X = \text{Transition Metal Derivative}$

Only two simple examples of this type of arsenical are known and they are formed by reacting the diarsine  $(\text{CF}_3)_2\text{As}-\text{As}(\text{CF}_3)_2$ , with the carbonyl compounds  $[(\pi\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3]_2$  and  $[(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$  (387).



On ultraviolet irradiation these compounds eliminate carbon monoxide and form the more usual arsenic-bridged derivatives.



The chemistry of these bridged complexes, which is outside the scope of this review, has been investigated by Hayter (388) and Chatt (389).<sup>3</sup>

## III

### PHYSICAL STUDIES

#### A. Structures

The structure of arsenic metal (390) with its directed valences,  $\text{As}-\text{As}-\text{As}$  angle  $97^\circ$ ,  $\text{As}-\text{As}$  distance of  $2.51 \text{ \AA}$ , and its infinite sheets of puckered six-membered rings, gives some idea of what is to be expected in the geometry of the largely covalent arsenic derivatives. In recent years the structures of a number of arsenicals have been determined by a variety of physical methods and those investigated by X-ray diffraction techniques are discussed first.

##### 1. Structures Determined by X-Ray Techniques

Triphenylarsine has been studied by several workers, the most recent investigation (391) confirming the earlier result that a complete structure determination of this molecule with eight molecules in a triclinic unit cell would be a difficult task. Happily, two other triarylarsines,  $(p\text{-tolyl})_3\text{As}$  and  $(p\text{-xylyl})_3\text{As}$  have simpler cells (391) and their structures are now known.

<sup>3</sup> See the article by Manuel in Volume III of this series.

The compounds are shown in Figs. 2 and 3 (392, 393). Both molecules have  $C_3$  symmetry showing the expected pyramidal structure with the lone pair presumably occupying the fourth coordination position round the arsenic.

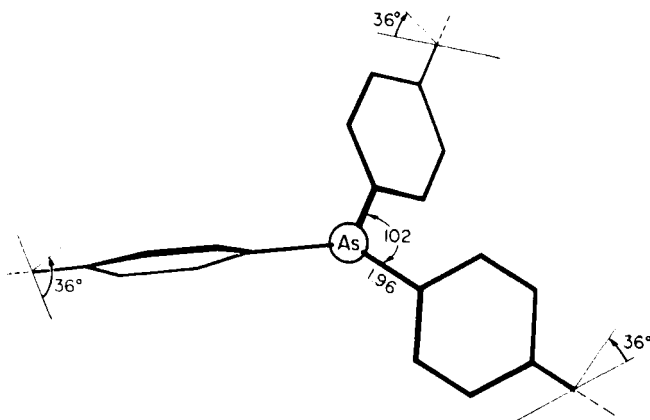


FIG. 2. The structure of  $(4\text{-CH}_3\text{C}_6\text{H}_4)_3\text{As}$ .

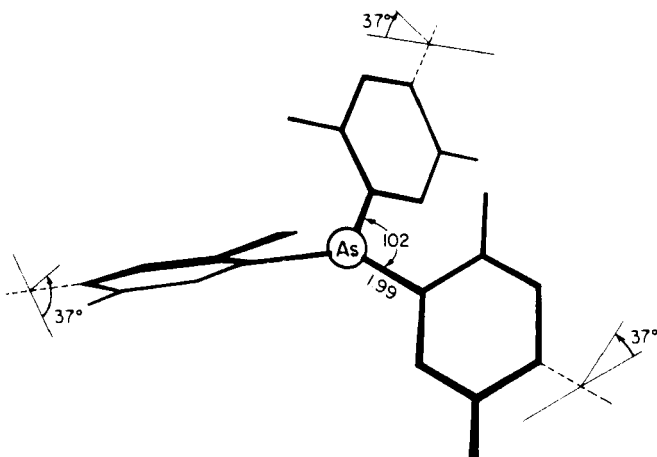


FIG. 3. The structure of  $[2,5\text{-(CH}_3)_2\text{C}_6\text{H}_3]_3\text{As}$ .

The phenyl rings are rotated  $36^\circ$  and  $37^\circ$  (the difference is not significant) from their positions in an ideal model which would allow maximum overlap of the  $\pi$  orbitals of the aromatic groups with the arsenic lone pair. The

direction of the lone pair is taken as that making equal angles with the bonds associated with the arsenic. The angle of rotation of the phenyl groups seems to be such as to make interactions between the lone pair and the aromatic rings as large as possible while increasing the nonbonded intramolecular contacts to the van der Waals distances. It is significant that a similar rotation in the case of the *p*-xylyl derivative is sufficient to relieve the more severe overcrowding involving the *ortho* methyl group.

The compounds  $(\text{C}_6\text{H}_5)_2\text{AsX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) are isomorphous but, as might be expected, the structure of the oxide,  $[(\text{C}_6\text{H}_5)_2\text{As}]_2\text{O}$ , is different (394). All four compounds have had their structures determined (395–398),

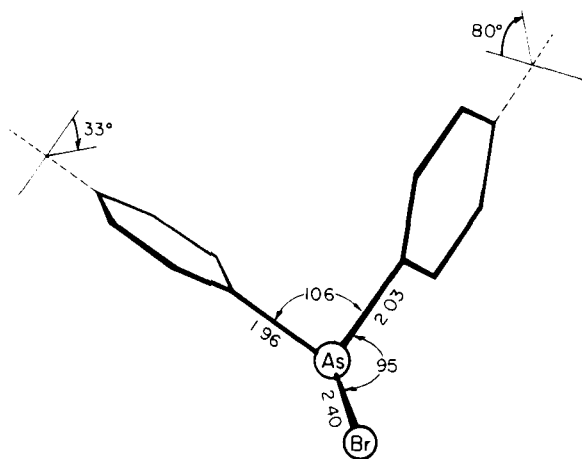


FIG. 4. The structure of  $(\text{C}_6\text{H}_5)_2\text{AsBr}$ .

and that of the bromide is shown in Fig. 4 (395). The most interesting feature of this molecule is the result that the phenyl groups are rotated to different extents from the ideal model position. The ring rotated  $36^\circ$  should be able to interact considerably with the arsenic lone pair. The other ring, rotated  $80^\circ$ , should have negligible interaction. In chlorodiphenylarsine the two rings are rotated  $35^\circ$  and  $76^\circ$  (396) and a similar situation is found in the iodo derivative (397). In the corresponding oxide, Fig. 5 (398), the carbon atoms were not located very precisely. Nevertheless, it was found that the two  $(\text{C}_6\text{H}_5)_2\text{As}$  groups are not identical and not related by any symmetry. The most significant feature of the oxide structure is the  $\text{As}-\text{O}-\text{As}$  angle of  $137^\circ$  which is considerably greater than the normal valency angle of oxygen, but is comparable with the value of about  $130^\circ$  found in  $\text{As}_4\text{O}_6$  (399). The

As—O distance of 1.67 Å in the oxide is, however, shorter than the 1.80 Å found in  $\text{As}_4\text{O}_6$  (399).

The simple alkyl arsenicals which have been investigated are  $(\text{CH}_3)_2\text{AsCN}$  (400),  $\text{CH}_3\text{AsI}_2$  (401), and  $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$  (402). The structure of the cyanide

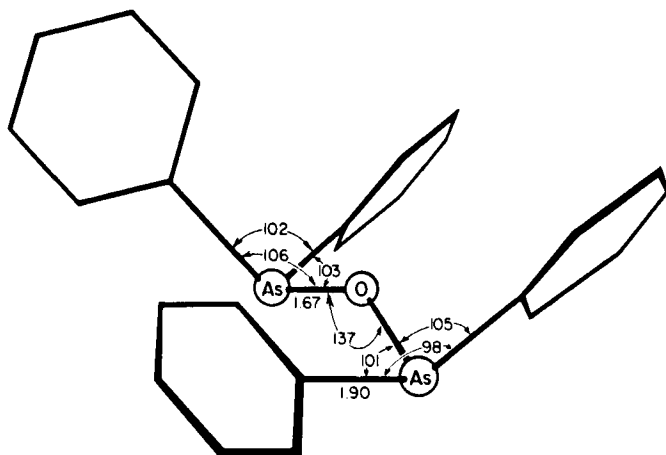


FIG. 5. The structure of  $[\text{C}_6\text{H}_5]_2\text{As}_2\text{O}$ .

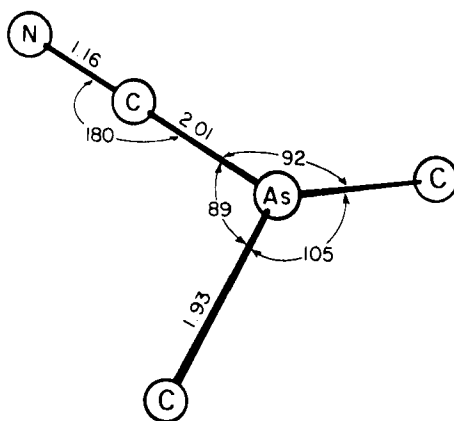


FIG. 6. The structure of  $(\text{CH}_3)_2\text{AsCN}$ .

was of interest because a number of compounds of the type  $(\text{CH}_3)_2\text{AsX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) had been investigated by electron diffraction (403). For these structures a  $\text{C—As—C}$  angle of  $96^\circ$  was assumed, this being the value found for  $(\text{CH}_3)_3\text{As}$  (404). The structure of the cyanide shown in Fig. 6 has

a much greater angle of  $105^\circ$  which is comparable with the similar angle in  $(\text{C}_6\text{H}_5)_2\text{AsBr}$  (Fig. 4). The two types of As—C distance present in the cyanide, As— $\text{CH}_3$  and As— $\text{C}\equiv\text{N}$ , are not significantly different. A very interesting feature of the cyanide structure is a very short As—N intermolecular contact of  $3.18 \text{ \AA}$ , which is considerably shorter than the sum of the van der Waals radii,  $3.5 \text{ \AA}$ . This distance suggests some sort of charge-transfer interaction, possibly involving the nitrogen lone pair and an arsenic  $4d$  orbital. Such an interaction could account for the fact that the cyanide is the only solid arsenical, at  $20^\circ \text{C}$ , of the type  $(\text{CH}_3)_2\text{AsX}$  ( $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{O}, \text{S}, \text{CF}_3, \text{C}_6\text{H}_5$ , etc.). Arsenic tricyanide also has a very short As—N

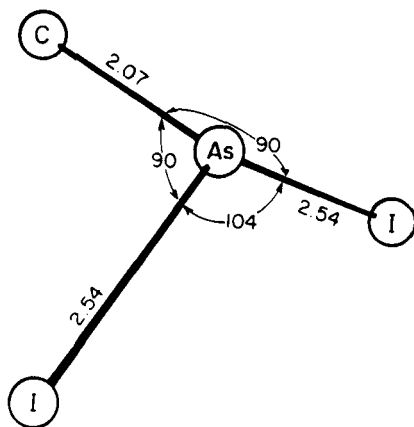


FIG. 7. The structure of  $\text{CH}_3\text{AsI}_2$ .

intermolecular distance (405). Diiodomethylarsine has a similar structure, Fig. 7 (401), although, because of heavy absorption, this was not determined very precisely.

The structure of  $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$  is shown in Fig. 8 (402). This compound, cacodyl disulfide, seems to have been assumed to have a disulfide link as in  $(\text{CH}_3)_2\text{As—S—S—As}(\text{CH}_3)_2$ . However, chemical evidence such as its formation from  $[(\text{CH}_3)_2\text{As}]_2\text{S}$  and  $\text{S}$ , was against such a formulation. The correct structure is in accord with the chemical properties of the compound (178, 402). The differences in the three As—S distances are significant, the short  $2.01\text{-}\text{\AA}$  bond indicating double-bond (or semipolar) character, and the  $2.21\text{-}\text{\AA}$  bond possibly indicating a smaller covalent radius for As(V) than for As(III). The As—S distances in  $\text{As}_4\text{S}_6$  and  $\text{As}_4\text{S}_4$  are  $2.25 \text{ \AA}$  and  $2.33 \text{ \AA}$

respectively (399), which correspond with the 2.28-Å distance in the disulfide. The differences in the As—C distances are not significant. The small and normal As—S—As angle should be compared with the large As—O—As angle of the oxide in Fig. 5. Similar angles in the disulfide structure do not have similar values. Thus the two  $\text{CH}_3\text{—As(V)=S}$  angles are  $115.7^\circ$  and  $111.9^\circ$ , the difference being ascribed to minor steric interferences. The angles at As(V) are approximately tetrahedral with those involving the “double-bonded” sulfur being greater than  $109^\circ$  and the others being less than this value. This result could be anticipated on the basis of a simple

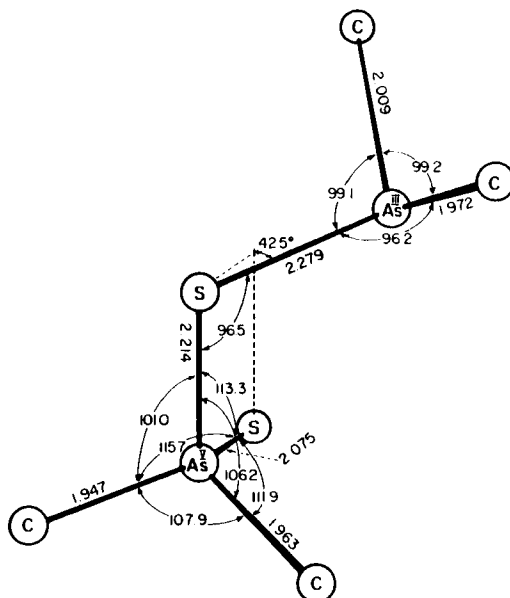


FIG. 8. The structure of  $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$ .

bond-pair lone-pair repulsion theory (406). In the crystal the molecules are associated in pairs with a short As(III)—As(V) separation of 3.24 Å and since the sum of the van der Waals radii is 4.0 Å this shortening could again indicate an intermolecular charge-transfer bond.

The approximately tetrahedral arrangement of the bonds around the As(V) in the disulfide structure becomes the exactly tetrahedral arrangement in  $(\text{C}_6\text{H}_5)_4\text{AsI}$  (407). The structure of this arsonium iodide consists of two interpenetrating body-centered lattices, one of  $(\text{C}_6\text{H}_5)_4\text{As}^+$  and the other of  $\text{I}^-$ . Each tetrahedral arsonium ion is surrounded by eight iodide ions at a

distance of 4.13 Å. The As—C distance is 1.95 Å and is not significantly different from the values found for compounds of the type  $R_3As$ . Tetramethylarsononium bromide consists of a tetrahedral  $(CH_3)_4As^+$  surrounded by four  $Br^-$  in an approximate Wurtzite structure (408). The As—C distance is about 1.9 Å and two closest As—Br distances of 4.18 and 4.01 Å are present. An ionic structure has also been described for  $(C_6H_5)_4AsI_3$  (409). A tetrahedral arrangement around arsenic is again present in the arylarsonic acids. The simplest,  $C_6H_5AsO(OH)_2$ , has been examined by two workers (410, 411) and although there are some differences in the two reported structures they are in agreement with the gross picture of an approximately tetrahedral arrangement round the arsenic. This arrangement gives rise to long chains

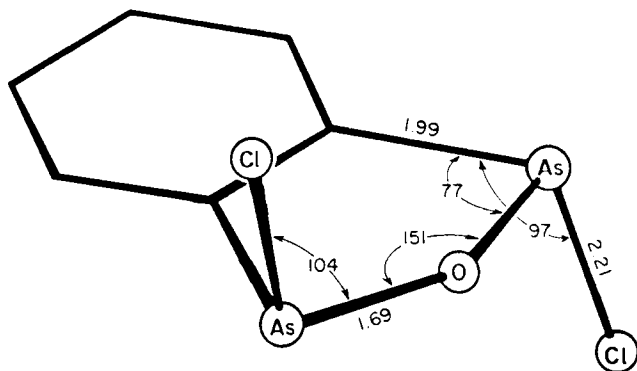


FIG. 9. The structure of *o*-phenylenediarsine oxychloride.

of molecules with the chains not directly bonded to each other. The molecules are held together by hydrogen bonds. The average As—O and As—C distances are 1.69 and 1.90 Å, respectively (411). Similar networks of hydrogen bonds are present in *o*- and *p*-aminobenzenearsonic acids (412, 413) and each molecule appears to have three hydrogen atoms bonded to the nitrogen, suggesting that the structure is that of the Zwitterion  $p$ - or  $o$ - $^+NH_3C_6H_4AsO_2(OH)^-$ . The As—O and As—C distances in these molecules appear to be in the usual range. The structure of dimethylarsinic acid  $[(CH_3)_2AsO(OH)]$  consists of centrosymmetrical hydrogen-bonded dimers (414).

The next group of arsenicals to be described contain arsenic in a ring system. The simplest of these, *o*-phenylenediarsine oxychloride, is shown in Fig. 9 (415). The five- and six-membered rings lie in one plane with one

chlorine up and the other down. The very interesting features of this molecule are the small C—As—O angle of  $77^\circ$ , the large As—O—As angle of  $151^\circ$ , and the short As—O distance. These values are best compared with those found for the oxide  $[(C_6H_5)_2As]_2O$  (Fig. 5). Five-membered rings containing arsenic seem to have a special stability (7) and the oxychloride is no exception. It has been suggested that in this case the molecule has some aromatic character, the shorter As—O distance being due to  $d\pi-p\pi$  bonding and the large As—O—As angle being the result of partial  $sp$  hybridization to facilitate this extra bonding. It might also be expected that further delocalization of electrons into the phenyl ring might occur which could result in a

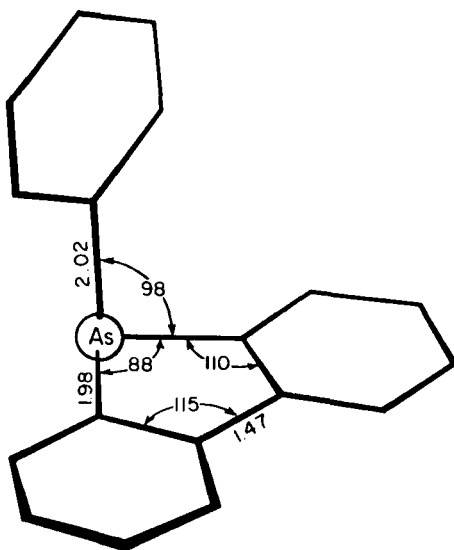


FIG. 10. The structure of 9-phenyl-9-arsafluorene.

shortening of the C—As bond. This distance, however, seems to be normal although it was not determined very accurately. A related molecule 9-phenyl-9-arsafluorene is shown in Fig. 10 (416). Again the arrangement of the bonds about the arsenic is pyramidal, and the valency angles at the arsenic are normal except for the internal C—As—C angle of  $88^\circ$ . The three rings of the arsafluorene unit are coplanar. The phenyl group is situated as shown occupying the position it would in the ideal model and the molecule has a plane of symmetry through the arsenic. Sartain and Truter (416) suggest that the phenyl group has this orientation because of better possibilities of overlap of arsenic  $d$  orbitals with the  $\pi$  orbitals on the biphenyl and phenyl



groups, although they indicate that there is no direct evidence for this. The expected shortening of the As—C bond is not observed since this has a length of  $1.98 \pm 0.02 \text{ \AA}^4$  within the five-membered ring.

Much interest has centered on the structure of compounds containing arsenic in a six-membered ring (see Section III, A, 3) and two of these have now been determined. Phenarsazine chloride, Fig. 11 (417), consists of two phenyl rings slightly folded about the As---N axis. The angle of fold is  $169^\circ$  and the chlorine atom is situated outside this angle. In addition to the folding, one and only one of the rings is slightly twisted so that the nitrogen

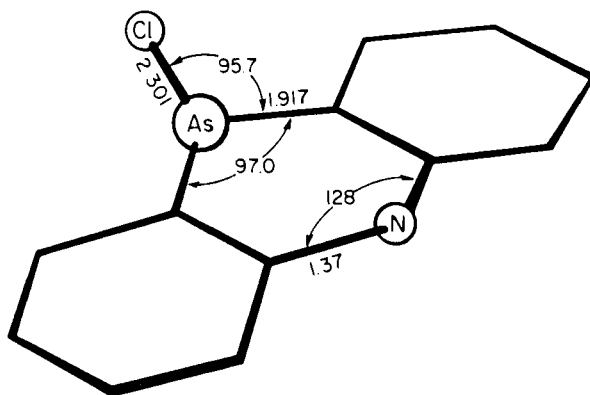


FIG. 11. The structure of phenarsazine chloride (10-chloro-5,10-dihydrophenarsazine).

and arsenic atoms do not lie in the plane of the ring. This twisting appears to be a result of crystal-packing forces. The As—Cl distance of  $2.30 \text{ \AA}$  is the same length as found in  $(\text{C}_6\text{H}_5)_2\text{AsCl}$  (396). However, the As—C distance, mean value  $1.917 \pm 0.007 \text{ \AA}^4$ , is significantly shorter than normal. One of the better values for this distance appears to be the  $1.99 \pm 0.019 \text{ \AA}^4$  found in  $[(\text{CH}_3)_2\text{As}]_2\text{S}_2$  (Fig. 8). The C—N distance,  $1.37 \text{ \AA}$ , is normal as is the external C—As—Cl angle. The C—As—C angle,  $97 \pm 0.4^\circ$ ,<sup>4</sup> is about what would be expected, however, the C—N—C angle of  $128^\circ$  is significantly larger than normal. The unusual features of this structure when taken together seem to indicate that the molecule could have an extended aromatic system involving the nitrogen lone pair, the arsenic lone pair (or *d* orbitals) and the  $\pi$  electrons of the phenyl groups.

The structure of the dibromide of 5,10-dihydro-5,10-dimethylarsanthrene is seen in Fig. 12 (418). The molecule is folded about the As---As

<sup>4</sup> Standard deviation.

axis and the angle between the planes is about  $157^\circ$ . The three C—As bonds about the pentavalent arsenic are probably coplanar. The upper bromine is displaced over the molecule such that the As—As—Br angle is  $76^\circ$ ; the lower one is displaced away from the molecule such that the As—As—Br angle is  $104^\circ$ . Thus the arrangement is similar to the trigonal bipyramidal structure found for  $(\text{CH}_3)_3\text{SbCl}_2$  and  $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$  (399) with the axial halogens displaced from their central position. This displacement, which is apparently a consequence of the folding of the molecule, results in a significant difference in the two As—Br bond lengths which are 2.59 and 2.66 Å, the longer bond being the one which has been “pushed out” due to the folding. The lengths of the As—Br bonds are much greater than the normal covalent distance, e.g., 2.40 Å in  $(\text{C}_6\text{H}_5)_2\text{AsBr}$  (Fig. 4). This axial

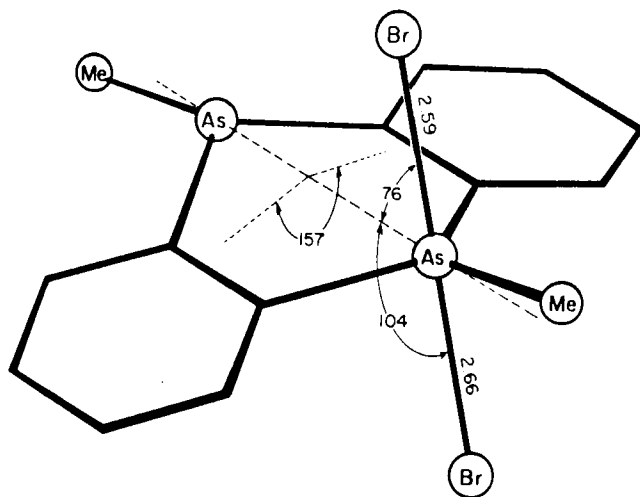


FIG. 12. The structure of the dibromide of 5,10-dihydro-5,10-dimethylarsanthrene.

lengthening is not unexpected in view of the long axial Sb—Cl bonds in the compounds  $(\text{CH}_3)_3\text{SbCl}_2$  and  $(\text{ClCH}=\text{CH})_3\text{SbCl}_2$ . The methyl group attached to the trivalent arsenic was not located very accurately though the arrangement around this arsenic atom seems to be pyramidal with an average intervalency angle of  $108^\circ$ . The structure of the corresponding diiodide of 5,10-dihydro-5,10-dimethylarsanthrene appears to be very similar though in this case only the heavy atoms were located (418). The two As—I distances are 2.80 and 2.98 Å.

Pentaphenylarsenic has been found to be isomorphous with pentaphenylphosphorus (419) although different from pentaphenylantimony which has the unusual square pyramidal arrangement of ligands. The initial communication suggested that the phosphorus and arsenic compounds also have a square pyramidal structure, however, since pentaphenylphosphorus has now been found to have the trigonal bipyramid structure (420) it can be expected that this arrangement also exists in pentaphenylarsenic.

Two very important structures shown in Figs. 13 and 14 are those of

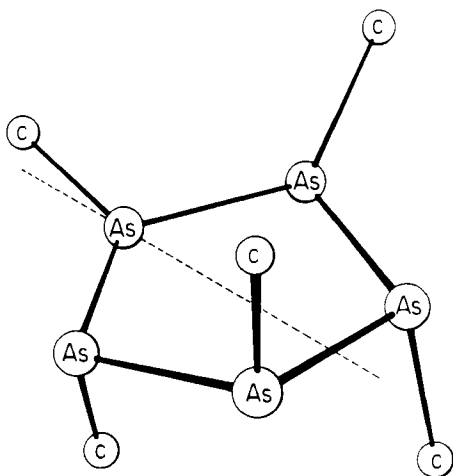


FIG. 13. The structure of arsenomethane,  $(\text{CH}_3\text{As})_5$ .

arsenomethane,  $(\text{CH}_3\text{As})_5$  (421) and arsenobenzene,  $(\text{C}_6\text{H}_5\text{As})_6$  (422, 423, 424). The methyl compound has a puckered five-membered ring of arsenic atoms. The mean As—As distance is 2.428 Å. In a planar molecule with equal angles and equal sides the As—As—As angle would be 108°, however, in  $(\text{CH}_3\text{As})_5$  these angles are unsymmetrically distorted to give an average value of 101.8°. The C—As—As angles are similarly distorted giving an average value of 96.9°. The ring of arsenic atoms almost has a mirror plane (dotted line in Fig. 13). As pointed out by Donohue (425) the structure of  $(\text{CH}_3\text{As})_5$  is remarkably similar to that of  $(\text{CF}_3\text{P})_5$ . Arsenobenzene has a six-membered ring of arsenic atoms in a chair form (424). The mean As—As—As and As—As—C angles are 91° and 100.1° but significant

deviations occur from these values. The mean As—C distance is 1.966 Å, which is not significantly different from other values notably the 1.95 Å found in  $(\text{CH}_3\text{As})_5$ . The mean As—As distance 2.456 Å is significantly longer than that found in  $(\text{CH}_3\text{As})_5$  (2.428 Å), although the values for arsenic metal (2.51 Å) (390) and  $\text{As}_4$  (2.44 Å) (426) are close. The reason for a five-membered ring in one case and a six-membered one in the other is obscure, although six-membered rings are found in arsenic metal (390).

The structures of the compounds  $(\text{C}_6\text{H}_5)_3\text{AsI}_2\text{Br}_2$  and  $(\text{C}_6\text{H}_5)_3\text{AsIBr}_3$  are under investigation. Both appear to contain the  $(\text{C}_6\text{H}_5)_3\text{AsBr}^+$  ion

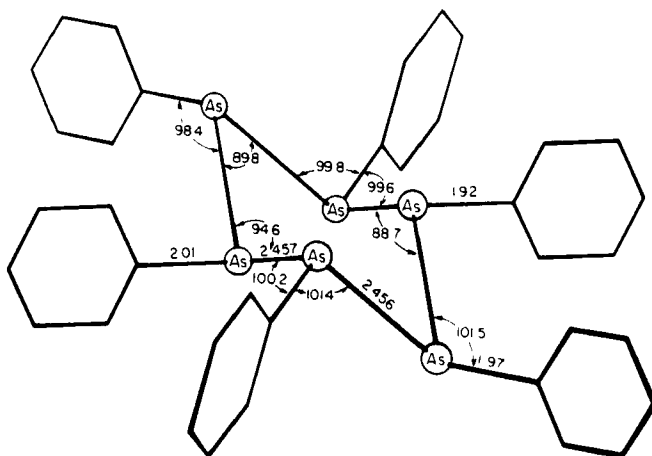


FIG. 14. The structure of arsenobenzene,  $(\text{C}_6\text{H}_5\text{As})_6$ .

associated with either  $\text{I}_2\text{Br}_2^-$  or  $\text{IBr}_2^-$  (427). These are the ions which are present in acetonitrile solutions of the two compounds (428).

## 2. Structures Determined by Other Techniques

Electron diffraction studies on trimethylarsine provided some of the first direct structural information about arsenicals. Springall and Brockway (404) found that this molecule has As—C distances of 1.98 Å and C—As—C angles of  $96^\circ \pm 5^\circ$ . The bond length is in good agreement with those determined by X-ray (Section III, A, 1) but the uncertainty in the angle leaves much to be desired. The  $C_{3v}$  symmetry of the molecule has been confirmed by a Raman study (429). A more recent microwave investigation of the same molecule (430) gives a value for the As—C bond of  $1.959 \pm 0.010$  Å, assuming a C—As—C angle of  $96^\circ \pm 3^\circ$ . The assumption of an angle of  $96^\circ$  and an

As—C distance of 1.98 Å was made in an electron diffraction study of the compounds  $(\text{CH}_3)_2\text{AsX}$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) (403). The values obtained for the bond lengths agree quite well with those obtained from other sources, as is shown in Table I.

TABLE I  
As—X BOND DISTANCES

X	As—X in $(\text{CH}_3)_2\text{AsX}$ (Å)	As—X from other simple molecules	References
Cl	2.18	2.16 in $\text{AsCl}_3$	403, 399
		2.26 in $(\text{C}_6\text{H}_5)_2\text{AsCl}$	396
Br	2.34	2.31 in $\text{AsBr}_3$	403, 399
		2.329 in $\text{AsBr}_3$	430a
		2.40 in $(\text{C}_6\text{H}_5)_2\text{AsBr}$	395
I	2.52	2.54 in $\text{AsI}_3$	403, 399
		2.556 in $\text{AsI}_3$	431
		2.53 in $(\text{C}_6\text{H}_5)_2\text{AsI}$	397
		2.54 in $\text{CH}_3\text{AsI}_2$	401

Diffuoromethylarsine ( $\text{CH}_3\text{AsF}_2$ ) has been studied by microwave spectroscopy (432) and the derived bond lengths and angles show no unusual features. An electron diffraction study of  $(\text{CF}_3)_3\text{As}$  indicates that the relatively bulky  $\text{CF}_3$  group has a normal value of  $100.1^\circ \pm 3.5^\circ$  for the C—As—C angle, however, the As—C distance is surprisingly increased to  $2.053 \pm 0.019$  Å (433). An older electron diffraction study of Lewisite showed that the main component is the *trans* isomer of  $\text{Cl}_2\text{AsCH=CHCl}$  (Section II, A, 9) (434). The length of the As—C bond is reported to be  $1.90 \pm 0.03$  Å, and the authors say that this shortening is due to the As—C=C group. This would seem to be unlikely in view of the greater, and normal lengths found for this bond in the phenyl arsenicals. However, a short bond is found in phenarsazine chloride (Fig. 11).

Triphenylarsine has been reported (435) to have a C—As—C angle of  $96^\circ$  as determined by electron diffraction. This value is much smaller than might be expected from the X-ray result of  $102^\circ$  for the same angle in similar molecules (Section III, A, 1). In Table II are given the values quoted for this particular angle.

TABLE II  
C—As—C ANGLES IN TRIVALENT ARSENICALS

Angle	Molecule	Method <sup>a</sup>	References
96°	(CH <sub>3</sub> ) <sub>3</sub> As	E	404
100°	(CF <sub>3</sub> ) <sub>3</sub> As	E	433
105°	(CH <sub>3</sub> ) <sub>2</sub> AsCN	X	400
99°	[(CH <sub>3</sub> ) <sub>2</sub> As] <sub>2</sub> S <sub>2</sub>	X	402
96°	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As	E	435
102° <sup>b</sup>	(4-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> ) <sub>3</sub> As	X	392
102° <sup>b</sup>	[2,5-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> ] <sub>3</sub> As	X	393
105°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsBr	X	395
105°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsCl	X	396
98°	9-Phenyl-9-arsafluorene <sup>c</sup>	X	416

<sup>a</sup> E, electron diffraction ; X, X-ray.<sup>c</sup> Exocyclic angle.<sup>b</sup> Mean values.

Values for the C—As—X angle are collected in Table III.

TABLE III  
C—As—X ANGLES IN TRIVALENT ARSENICALS

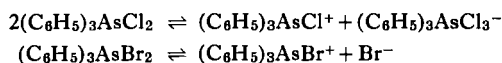
X	Angle	Molecule	Method <sup>a</sup>	References
F	96°	CH <sub>3</sub> AsF <sub>2</sub>	M	432
Cl	98°	(CH <sub>3</sub> ) <sub>2</sub> AsCl <sup>b</sup>	E	403
Br	96°	(CH <sub>3</sub> ) <sub>2</sub> AsBr <sup>b</sup>	E	403
I	98°	(CH <sub>3</sub> ) <sub>2</sub> AsI <sup>b</sup>	E	403
Cl	96°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsCl	X	396
Br	95°	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> AsBr	X	395
Cl	97°	<i>o</i> -Phenylenediarsine oxychloride	X	415
Cl	96°	Phenarsazine chloride	X	417
S	99°	[(CH <sub>3</sub> ) <sub>2</sub> As] <sub>2</sub> S <sub>2</sub> <sup>c</sup>	X	402
S	96°	[(CH <sub>3</sub> ) <sub>2</sub> As] <sub>2</sub> S <sub>2</sub> <sup>c</sup>	X	402
I	90°	CH <sub>3</sub> AsI <sub>2</sub>	X	401

<sup>a</sup> M, microwave ; E, electron diffraction ; X, X-ray.<sup>b</sup> Assumed C—As—C angle = 96°.<sup>c</sup> Two values not equivalent (see Section III, A, 1).

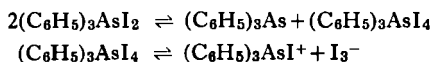
Dipole moment measurements in conjunction with a knowledge of the molar Kerr constants and refractivities have been used (436) to calculate the rotation of the phenyl groups of triphenylarsine from their position in the ideal model (Section III, A, 1). In benzene solution, assuming a value of  $96^\circ$  for the C—As—C angle (435), the rotation is calculated to be  $37^\circ \pm 3^\circ$ . Using the more likely value of  $102^\circ$  the angle of rotation is found to be  $40^\circ \pm 3^\circ$  (437). Both values are in agreement with what could be expected from the available data (Section III, A, 1).

The correct structure of the isomers present in Lewisite was first proposed as a result of dipole moment studies (438). The moment of the main component, *trans*-CHCl=CHAsCl<sub>2</sub>, was found to be  $2.21 \times 10^{-18}$  esu in benzene at  $25^\circ$  and that of iso-Lewisite, the *cis* compound, to be  $2.61 \times 10^{-18}$  esu. The greater value for the *cis* compound is perhaps the most reliable criterion of structure although in the original paper calculations of moments based on assumed structures were offered as evidence. Because of the uncertainty in these calculations and the small difference in the experimental moments the structure of Lewisite was redetermined, and verified, by electron diffraction (434) as mentioned above.

Triphenylarsenic dichloride [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsCl<sub>2</sub>] is reported to probably have a dipole moment of zero (439) which would indicate a trigonal bipyramidal structure with the phenyl groups equatorial. This same structure has been suggested for the compounds (C<sub>6</sub>H<sub>5</sub>)<sub>n</sub>AsF<sub>5-n</sub> ( $n = 1, 2, 3$ ) (440). The tetrafluoride, C<sub>6</sub>H<sub>5</sub>AsF<sub>4</sub>, shows only one peak in its <sup>19</sup>F NMR spectrum, possibly due to fast intramolecular fluorine exchange. The trifluoride, (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>AsF<sub>3</sub>, gives the expected doublet and triplet of relative intensity 2:1, the spectrum being consistent with a slightly distorted trigonal bipyramidal structure with equatorial aryl groups. The difluoride shows only one peak whose position is relatively insensitive to solvent or concentration. In solution in acetonitrile however, conductance studies show that the dihalides (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>AsX<sub>2</sub> (X = Cl, Br, I) exhibit a surprising range of behavior (428, 441). The chlorides and bromides ionize as follows:



and the iodide disproportionates to the tetraiodide which then ionizes.

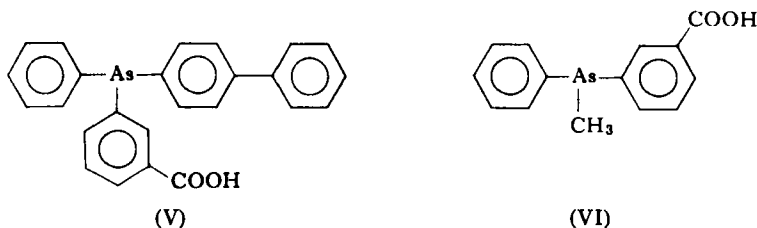


Spectroscopic studies in acetonitrile support this ionization scheme for the diiodide, however, in carbon tetrachloride and dichloromethane solution it seems to be a charge transfer complex (441a).

### 3. Structural Information from Optical and Geometrical Isomerism

a. *Acyclic Compounds*<sup>5</sup>. Once it was realized that the failure to resolve derivatives of nitrogen was due to the high frequency of inversion (442), attention was given to the problem of resolving simple derivatives of the type  $R_3M$  ( $M = P, As$ ). Calculations of the frequency of inversion of the pyramidal molecules  $H_3As$  and  $D_3As$  led to the suggestion (443) that substitution of large groups in place of the hydrogen "might produce a molecule for which the frequency of inversion is sufficiently slow to enable optically active isomers to be separated at low temperatures." Weston (444) later calculated that at  $107^\circ C$  the half-time for racemization of  $(CH_3)_3As$  is 2 hours. But in spite of this Kamai in a series of papers (e.g., 65, 445) described the preparation and unsuccessful resolution of a number of compounds of the type  $RR'As(R''COOH)$ , one of  $R$  or  $R'$  being an alkyl group. He used the carboxyl group as a handle to prepare salts of alkaloids such as strichnine and cinchonine.

Recently the triaryarsine, *p*-biphenyl-*(m*-carboxyphenyl)phenylarsine (V)



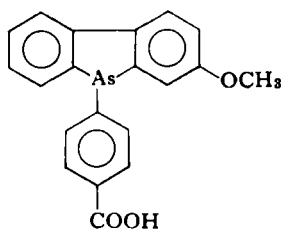
was resolved using  $(-)\text{-}\alpha\text{-phenylethylamine}$  to obtain the  $(+)\text{-arsine}$ , and  $(+)\text{-amphetamine}$  to obtain the  $(-)\text{-arsine}$  (446). This success followed the resolution of a similar triarylstibine (447). An alkyldiaryarsine investigated by Kamai (448) (VI) has been reinvestigated with respect to resolution but without success (449). In the light of the successful resolution of the triaryarsine (V) this failure has been attributed to insufficient difference in solubilities of the corresponding diastereomeric salts, or to a very low optical rotation of the enantiomers, or both.

<sup>5</sup> Compounds of the type  $R_3As$  where the As is not part of a ring system.

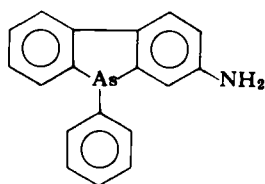


Optically active arsines containing alkyl groups have recently been prepared by electrolytic reduction of optically active quaternary arsonium salts (450). The optically active arsine combines with sulfur in benzene to give the active arsine sulfide.

b. *Cyclic Arsines*. The stability of the arsenic pyramid has also resulted in the resolution of arsafluorene derivatives. Thus Campbell and Poller were able to separate 9-*p*-carboxyphenyl-2-methoxy-9-arsafluorene (VII) and 2-amino-9-phenylarsafluorene (VIII) into optical enantiomers (451).

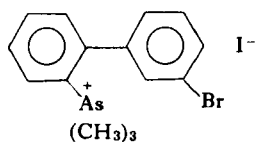


(VII)

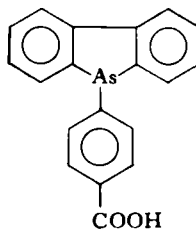


(VIII)

Since a nonplanar arsafluorene unit would also lead to optical activity, giving derivatives of biphenyl like 3'-bromobiphenyl-2-trimethylarsonium iodide (IX)



(IX)

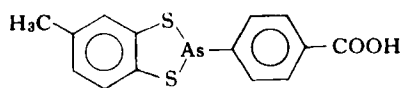


(X)

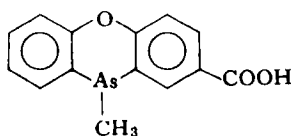
which had previously been partly resolved (144), the resolution of 9-*p*-carboxyphenyl-9-arsafluorene (X) was attempted (451). This was not successful, indicating that the arsafluorene unit is planar and that the optical activity is due to the stable configuration around the arsenic. The geometry of this type of molecule has since been confirmed by X-ray measurements (Section III, A, 1).

Another pyramidal molecule containing a five-membered ring, 2-*p*-carboxyphenyl-5-methyl-1,3-dithia-2-arsindane (XI) has also been resolved

(452). This arsindane, like the arsafluorenes, shows considerable optical stability.

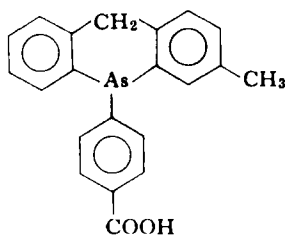


(XI)

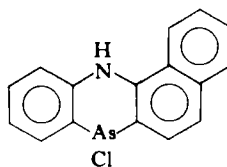


(XII)

The very first arsine to be resolved was a phenoxarsine derivative, 10-methyl-phenoxarsine-2-carboxylic acid (XII), and this was also optically stable (453). Lesslie and Turner suggested two models to explain this result. In the first the molecule is considered to be *stably folded* about the As—O axis and thus would exhibit optical activity irrespective of the position of the methyl group. In the second the molecule is planar, the methyl group being situated above or below the plane in a *stable* position. They favored the first model and suggested that the angle of fold would be greater than 150°. The corresponding 10-ethyl and 10-phenyl compounds have been resolved as also has 10-*p*-carboxyphenyl-2-chlorophenoxarsine (454). A related molecule 2-methyl-10-(*p*-carboxyphenyl)-5,10-dihydroarsacridine (XIII) has also been resolved (446) demonstrating that the oxygen has little to do with the resolution of the phenoxarsines.



(XIII)



(XIV)

Allen and Wells (455) had previously reported the resolution of a phenarsazine derivative, the bromocamphorsulfonate formed from (XIV), although this work has been questioned (7, 453).

Two forms of 5,10-di(*p*-tolyl)-5,10-dihydroarsanthrene have been isolated by fractional crystallization from acetone (456). Both forms give the same tetrabromide. From consideration of molecular models Chatt and Mann concluded that the dihydroarsanthrene system would be folded about

the As---As axis and consequently geometric isomers would be possible as shown in Fig. 15. They concluded that the first two forms are those of the

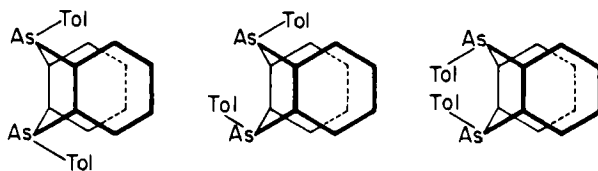


FIG. 15. Geometric isomers suggested for 5,10-di-*p*-tolyl-5,10-dihydroarsanthrene.

isomers isolated, the third form, looked for but not found, being too crowded to exist.

Thus geometrical isomerism in the dihydroarsanthrenes has been attributed to a stable folding of the molecule *and* a stable arsenic pyramid. The optical isomers in the phenoxarsines have been attributed to a stable folding of the molecule but not necessarily associated with a stable arsenic pyramid although this seems to have been implied. The structure of

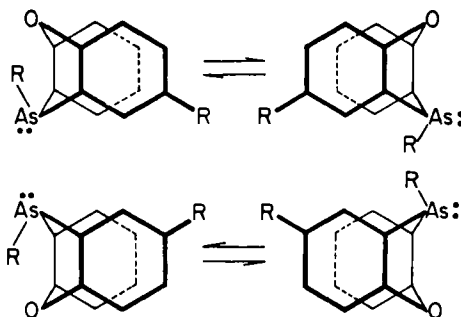


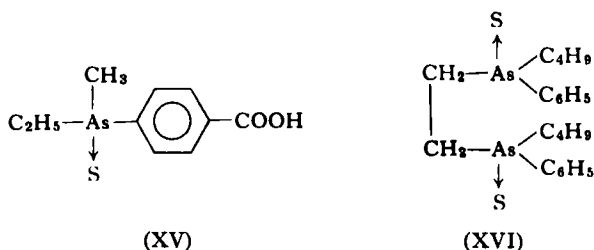
FIG. 16. Two isomers of a resolvable phenoxarsine. It is suggested that these exist in solution as mixtures of rapidly interconverting diastereomeric folded conformations.

phenarsazine chloride and of the dibromide of 5,10-dihydro-5,10-dimethylarsanthrene (Section III, A, 1) indicates that molecules of this type are folded in the solid state. The resolution of acyclic arsines indicates that the arsenic pyramid is stable and the question arises as to whether these cyclic molecules are in fact stably folded. Mislow *et al.* (446) have calculated that for this type of molecule the barrier to folding via a planar transition state, with retention of configuration around the arsenic, is of the order of 7 kcal/mole. They conclude that "it seems inconceivable that 5,10-dihydroarsanthrenes and similar molecules are stably folded." They do however

concede that "special factors, such as very large 5,10-substituents, may lead to a situation where one of the two diastereomeric *exo* and *endo* isomers of the *cis* form exists as by far the most populous component in the mobile conformational equilibrium." The type of situation suggested for phenoxarsines is thus pictured as in Figure 16. A Dreiding model study by Davis and Mann (456a, 457) also indicates that the dihydroarsanthrenes probably exist as butterfly conformations which readily interconvert. However, as pointed out by Mislow *et al.* (446) the possibility that these tricyclic systems are planar in solution cannot be rigorously excluded (see (XII) and related discussion).

### 3. Arsenicals Coordinated by Four and Five Groups

The class of four-coordinate arsenic compounds was the first to be resolved, the arsine sulfide, (XV) having been studied by Mills and Raper (458).



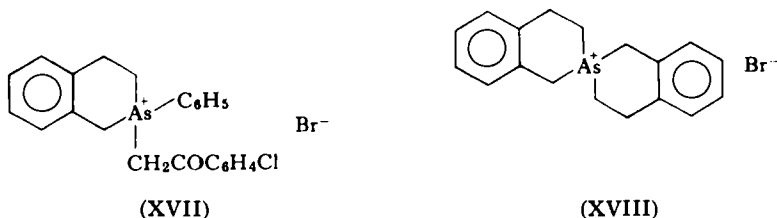
A similar compound, the disulfide of ethylene-1,2-bis(*n*-butylphenylarsine) (XVI) was separated into two isomers m.p. 113°–116° C and 121° C respectively (375). The lower melting form can be converted into the other by heating, and since the two isomers are probably the *meso* and racemic forms, the configuration at only one arsenic is altered. Although the mechanism of the conversion is not known it has been suggested (10, 375) that the change can take place because of the existence, in the molten solid, of an equilibrium between the disulfide and the corresponding mono-sulfide. It has already been mentioned above that optically active arsines react with sulfur to give optically active arsine sulfides (450).

Arsonium compounds are also four-coordinated and many attempts have been made to resolve suitable derivatives. Most of the early attempts were failures because the "onium" compounds contained alkyl groups which easily take part in equilibria such as  $R_3As^+R' + I^- \rightleftharpoons R_3As + R'I$ , thus

causing racemization. An interesting sidelight on this dissociation equilibrium is that methyl iodide catalyzes the racemization of arsafluorene derivatives such as (VII) above (451).

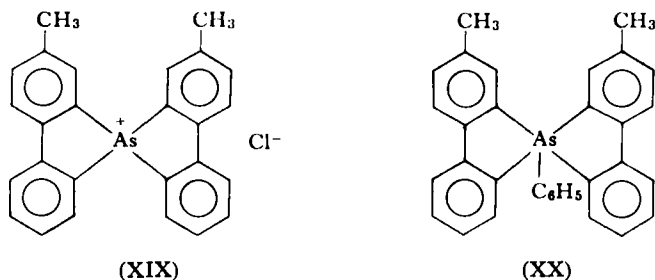
Resolution of alkyl-containing arsonium compounds has recently been achieved using conventional techniques (450, 459). However, a more interesting method involves resolution by asymmetric adsorption on natural dissymmetric adsorbants such as *d*- and *l*-quartz and (+)- and (-)-lactose (460, 461). The time for complete racemization of the arsonium compounds is of the order of 70 minutes.

Holliman and Mann (462, 463), taking advantage of more stable systems, had earlier resolved compounds (XVII) and (XVIII) via their *d*-bromocamphorsulfonates.



Mann *et al.* (464) have also resolved a number of other spiro and normal arsonium compounds of this type, with the notable exception of tetraarylarsonium salts with four dissimilar aryl groups (113). The over-all evidence in conjunction with the known structures (Section III, A, 1) provides convincing evidence for the more or less tetrahedral arrangement adopted by four groups attached to an arsenic atom.

The spiro compound (XIX) has also been resolved (86) and both forms react with phenyllithium to give the same product (XX).



#### 4. *Structural Information from Molecular Weight*

The molecular weights of a number of arsenicals have been determined in solution. The general situation with respect to aryl derivatives has been summarized by Blicke and Smith (329). They divide the compounds into three groups. Group I contains compounds in which the arsenic is linked by a single bond to another atom, not arsenic. These have normal molecular weights, for example,  $(\text{C}_6\text{H}_5)_3\text{As}$ ,  $[(\text{C}_6\text{H}_5)_2\text{As}]_2\text{O}$ ,  $\text{C}_6\text{H}_5\text{AsCl}_2$ . Group II contains arsenic "double-bonded" to another atom. These compounds do not react with oxygen under ordinary conditions and in solution are associated, for example,  $(\text{C}_6\text{H}_5\text{As}=\text{AsC}_6\text{H}_5)_3$ ,  $(\text{CH}_3\text{As}=\text{AsCH}_3)_{24}$ . Group III contains molecules with As—As single bonds which react instantly with oxygen under ordinary conditions. They have mostly normal molecular weights though in solution they could be slightly dissociated, for example,  $(\text{C}_6\text{H}_5)_2\text{As}-\text{As}(\text{C}_6\text{H}_5)_2$ . The oxides  $\text{C}_6\text{H}_5\text{AsO}$  and  $(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)\text{AsO}$  can apparently exist as a higher polymer (209a, 324). Some other determinations of the degree of association of  $\text{RAsO}$  and  $\text{RAsS}$ -type compounds indicate that this can be three (347) and even two as in  $[(\text{C}_5\text{H}_5\text{FeC}_5\text{H}_4)\text{AsO}]_2$  (209a, 347).

In the vapor state, at  $200^\circ\text{C}$ , arsenomethane has a molecular weight corresponding to that of the pentamer,  $(\text{CH}_3\text{As})_5$  (465), found in solution and by X-ray (Section III, A, 1). At  $270^\circ\text{C}$  the species present is apparently  $(\text{CH}_3\text{As})_3$ . Vapor-phase molecular weights of other arsines are normal and the diarsine  $(\text{CF}_3)_2\text{As}-\text{As}(\text{CF}_3)_2$  shows no sign of dissociation at ordinary temperatures (28a).

### B. *Spectroscopic Properties*

#### 1. *Raman, Infrared, NMR, and ESR Studies*

Raman spectra have been reported for  $(\text{CH}_3)_2\text{AsX}$  and  $\text{CH}_3\text{AsX}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) and in the case of the chlorides have been interpreted in terms of a decreasing As—Cl distance as  $\text{CH}_3$  is replaced by Cl (466). The Raman spectrum of  $(\text{CH}_3)_4\text{AsCl}$  in aqueous solution is consistent with a tetrahedral ion (467). Raman data are also available for  $(\text{CH}_3)_3\text{As}$ ,  $\text{CH}_3\text{AsO}(\text{OH})_2$ , and  $(\text{CH}_3)_2\text{AsO}(\text{OH})$  (429, 467, 468, 469).

In recent years the infrared spectra of a number of arsines and arsonium compounds have been published and some correlations and assignments have been made (470–473d). It has been found (473b, 473c, 473d) that the  $\text{CH}_3-\text{As}$  stretching, methyl rocking, and methyl deformation frequencies

TABLE IV  
COMPARISON OF SOME FUNDAMENTAL FREQUENCIES (CM<sup>-1</sup>) OF SOME ALKYLARYLARSINES  
AND ALKYLARYLARSONIUM COMPOUNDS

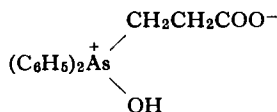
Fundamental	(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>5</sub> As	(CH <sub>3</sub> ) <sub>3</sub> C <sub>6</sub> H <sub>5</sub> As <sup>+</sup>	CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> As	(CH <sub>3</sub> ) <sub>2</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> As <sup>+</sup>	(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As	CH <sub>3</sub> (C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> As <sup>+</sup>
$\nu(\text{CH}_3\text{---As})^a$	575	632	574	627	—	625
CH <sub>3</sub> rock	889	924	837	926	—	892
	847	853	—	893	—	—
	—	843	—	843	—	—
CH <sub>3</sub> sym. def.	1258	1268	1247	1268	—	1280
	1242	—	—	—	—	—
CH <sub>3</sub> stretch	2980	3000	2993	3010	—	3000
	2915	2916	2912	2920	—	2919
X-sensitive $q$	1079	1090	1081	1091	1074	1085
	—	—	—	1087	—	—
$r$	671	(690) <sup>b</sup>	672	(690) <sup>b</sup>	667	683
	667	—	668	680	—	—
$t$	295	304	310	329	310	342
	—	—	298	304	—	302

<sup>a</sup> Weighted average. See Ref. 473c.

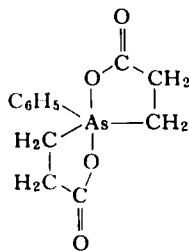
<sup>b</sup> Probable position, obscured by strong band.

all increase when the arsines  $(\text{CH}_3)_n\text{As}(\text{C}_6\text{H}_5)_{3-n}$  ( $n = 1-3$ ) form the arsonium ions  $(\text{CH}_3)_{n+1}\text{As}^+(\text{C}_6\text{H}_5)_{3-n}$ . This implies an increase in the strength of the C—As bond on 'onium salt formation. The X-sensitive modes of the phenyl groups of the arsines also shift to higher wavenumbers which is in accord with an increase in the strength of the  $\text{C}_6\text{H}_5\text{—As}$  bond. There is very little change in the C—As stretching frequency of  $(\text{CH}_3)_4\text{As}^+$  when the  $\text{CH}_3$  groups are replaced by phenyl. These trends are shown in Table IV (473c). It is worth noting that the C—H bond of the  $\text{CH}_3$  group also seems to be stronger in the arsonium compounds.

Compounds containing the grouping  $\text{As}(\text{O})\text{OH}$  usually have three broad bands near  $2600$ ,  $2200$ , and  $1700\text{ cm}^{-1}$  (474) although in some instances the  $1700\text{-cm}^{-1}$  band is missing or ill-defined. A study of the spectra of aliphatic carboxylic acids containing arsenic led Brauholtz and Mann (475) to suggest that whereas the acid  $\text{C}_6\text{H}_5\text{As}(\text{O})(\text{CH}_2\text{COOH})_2$  has a normal structure the compound  $(\text{C}_6\text{H}_5)_2\text{As}(\text{O})\text{CH}_2\text{CH}_2\text{COOH}$  exists as the Zwitterion (XXI).



(XXI)



(XXII)

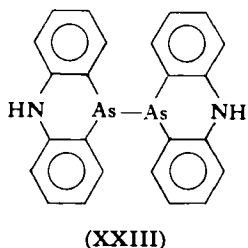
They also give chemical and spectroscopic evidence that the oxidation product of the acid  $\text{C}_6\text{H}_5\text{As}(\text{CH}_2\text{CH}_2\text{COOH})_2$ , is a dicyclic dihydroxide dilactone for which they suggest the structure (XXII). Infrared spectroscopy has also been used to show that triethylarsine forms an intermolecular hydrogen bond with methanol (476).

Nuclear magnetic resonance (NMR) spectra have also been reported for a number of arsenicals but little attention has been given to the effects of the arsenic. Studies on the chemical shifts of  $(\text{CH}_3)_3\text{As}$  and related compounds seem to indicate that this is related to the polarity of the M—C bond. The suggested electronegativities arising from this work (477, 478) are as follows:  $\text{N} (3.04) > \text{P} (2.19) = \text{As} (2.18) > \text{Sb} (2.06) < \text{Bi} (2.16)$ . The



NMR spectra of  $(C_2H_5)_3As$  and  $(C_2H_5)_4AsBr$  and related molecules have been measured in a number of solvents (479, 479a). The spectra of the arsonium compounds are broad in ionizing solvents and this is taken as indicating spin coupling of the protons with the arsenic atoms. It seems that in the ethyl compound  $J_{CH_3-As} < J_{CH_3-As}$ . In chloroform solution the spectrum is sharp indicating ion-pair formation. The  $^{19}F$  spectra of compounds such as  $(C_6H_5)_3AsF_2$  have been discussed with respect to the structure of pentacoordinated arsenicals in Section III, A, 2. An example of the use of NMR in establishing the structure of reaction products is given in Section II, A, 9, a (Fig. 1).

ESR spectroscopy has been applied only in a very few instances to organo-arsenic compounds. The diarsine (XXIII) has been shown to be diamagnetic (480) and a preliminary investigation (481) of the reaction of



arsenobenzene with lithium (Section II, C, 2) failed to find the free radicals postulated previously as intermediates (217). There are, nevertheless, quite a few reactions and products which could be profitably studied by this technique including, for example, the intensely colored compounds obtained by reducing phenarsazine chloride. The species produced is reported to have a magnetic moment of 1.72 Bohr magnetons indicating one unpaired electron (482). Ion radicals are also believed to be produced when tris(*p*-dimethylaminophenyl)arsine is oxidized (483). A recent investigation of a radical obtained by oxidation of a phenol derivative, 4-OH-3,5-(*tert*- $C_4H_9$ ) $_2C_6H_2As(S)(C_6H_5)_2$ , shows that the  $^{75}As$  nucleus (spin, 3/2) interacts with the unpaired electron (483a).

## 2. Ultraviolet Spectra

The first report on the UV spectra of arsenicals was part of a study of chemical warfare materials made by Mohler and his co-workers (484). However, the spectra do not seem to be very reliable.

A number of compounds of the type  $C_6H_5M(CH_3)_2$  ( $M = N, P, As, Sb$ ) were studied by Bowden and Braude (485) and they observed a big difference in the spectrum of the arsine compared with that of the corresponding arsonium compound  $C_6H_5As(CH_3)_3I$ . The latter has a spectrum very similar to benzene. The difference in spectra was ascribed to the presence of the lone pair on the arsenic in the case of the arsine and its absence in the arsonium compound. The same observation was made by Mann *et al.* (81) with respect to the spectra of triphenylarsine and its methiodide.

Jaffé studied compounds of arsenic not having lone pairs and suggested

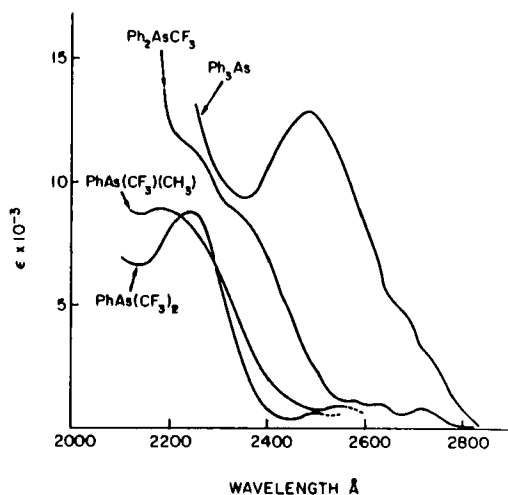


FIG. 17. The ultraviolet spectra of some phenylarsines.

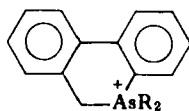
that no resonance interaction is encountered between several phenyl radicals attached to the central atom, and that each phenyl radical makes an independent contribution to the absorption (486). In molecules with an unshared pair, however, Jaffé concluded that extensive conjugation between the phenyl radicals and the metal atom occurs, leading to a complete change in the  $\pi$ -electron system and hence a complete change in the spectrum from that of benzene and its simple derivatives. Rao *et al.* (471) have discussed similar spectra using similar ideas.

The spectra of some arylarsines are shown in Figure 17; of especial interest is the broad band of  $(C_6H_5)_3As$  which shows some structure on the low-energy tail (487). This band is solvent-sensitive, being red-shifted

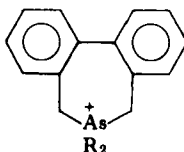
(lower energy) on changing solvent from a polar to less polar medium, and blue-shifted (higher energy) when the solvent is changed from nonpolar to polar. Indeed, when trifluoroacetic acid is the solvent the band moves far enough to the blue that the band system producing the structure on the low-energy tail becomes quite distinct. Furthermore, on replacing the  $\text{C}_6\text{H}_5$  groups by electronegative  $\text{CF}_3$  groups the main band is blue-shifted and again a weaker band system appears at lower energies. It seems that the low-energy bands are best explained as benzene type  $\pi-\pi^*$  transitions and the more intense solvent-sensitive bands are explained in terms of absorption to states having partial intramolecular charge-transfer character, that is, transitions involving the arsenic lone pair and a benzene ring. It is possible to calculate the spectra expected from the arylarsines and the results indicate that this charge-transfer model is appropriate (488). The calculated spectrum is very sensitive to changes in the ionization potential of the arsenic lone pair and thus it is very sensitive to solvent and substituent effects.

Two higher energy bands are present in the spectrum of  $(\text{C}_6\text{H}_5)_2\text{AsCF}_3$ , Fig. 17, and these have been explained on the basis of the two phenyl rings being nonequivalent due to interaction of one of the rings with the fairly bulky  $\text{CF}_3$  group. The interacting ring, possibly hydrogen-bonded, is thus stabilized and models indicate that it would be held in a position close to the ideal one for maximum overlap, the other ring would consequently be twisted almost  $90^\circ$  from the ideal position. The situation envisaged is similar to that subsequently found in  $(\text{C}_6\text{H}_5)_2\text{AsBr}$  (Fig. 4, Section III, A, 1). Very similar spectra are obtained for the compounds  $(\text{C}_6\text{H}_5)_n\text{AsX}_{3-n}$  and  $\text{C}_6\text{H}_5\text{As}(\text{CH}_3)_n\text{X}$  ( $\text{X} = \text{CF}_3, \text{C}_3\text{F}_7$ ;  $n = 0, 1, 2$ ) but in general the charge-transfer band occurs at higher energies for the  $\text{C}_3\text{F}_7$  compounds indicating that, other things being equal, the effect of the  $\text{C}_3\text{F}_7$  group on the arsenic lone-pair (electron-withdrawing power) is greater than that of the  $\text{CF}_3$  group (69). It is important to note that the presence of the weak  $\pi-\pi^*$  bands in the spectra of the arylarsines indicates that the  $\pi$ -orbital configuration in the benzene rings is not greatly different in these compounds from that in simple monosubstituted benzenes and that there is therefore little or no conjugative interaction between the arsenic atom and the benzene rings, or between the benzene rings.

In addition to the arsafluorenes the UV spectra of a number of other 2-biphenyl and 2,2'-bridged biphenyl derivatives of arsenic have been studied (205, 489, 490, 491) but in most of these the arsenic was present either as arsonium ions as in (XXIV) or (XXV) or in the pentavalent state.

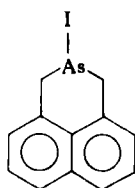


(XXIV)

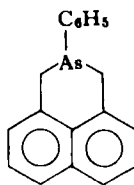


(XXV)

Consequently, the spectra resemble those of the corresponding hydrocarbons and can be similarly interpreted. The charge-transfer model also accounts for the similarity of the spectra of (XXVI) and the methiodide of (XXVII) (213) since the phenyl group of the latter compound would add only weak benzene type bands to the spectrum of (XXVI), the arsenic atom



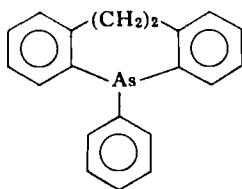
(XXVI)



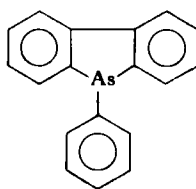
(XXVII)

in this case being too far away from the naphthalene group, two bonds, to contribute much to the spectrum. Even when the arsenic atom is one bond away as in the  $\alpha$ -naphthyl arsines the spectrum seems to be little altered from that of a simple monosubstituted naphthalene (492).

Using the charge-transfer model it is not difficult to account for the similarity of the spectrum of (XXVIII) with that of  $(\text{C}_6\text{H}_5)_3\text{As}$  and the lack of similarity with (XXIX). However, Campbell and Poller (489) attribute



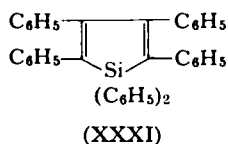
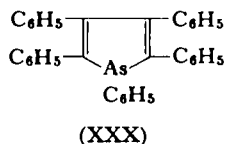
(XXVIII)



(XXIX)

the difference in spectra to a bathochromic shift of the main band of triphenylarsine (247  $\text{m}\mu$ ,  $\epsilon = 13,100$ ) to 279  $\text{m}\mu$  ( $\epsilon = 14,100$ ) in the

arsafluorene. They take this as indicating considerably increased conjugation between the hetero atom and the condensed ring system. There is little evidence for this conclusion. A related molecule pentaphenylarsole



(XXX) has a UV spectrum similar to the corresponding phosphole and to the silicon analog (XXXI) (84), indicating little aromatic character. Brown has suggested that conjugation could occur in the arsole (493).

The UV spectra of arsenobenzene,  $(\text{C}_6\text{H}_5\text{As})_6$ , arsono-*p*-toluene, and arsono-*m*-toluene have been described (494). They show a band in the region of  $250 \text{ m}\mu$ , which is probably due to charge transfer, and another at  $315 \text{ m}\mu$ . The lower energy band has been tentatively assigned to a transition involving a nonbonding electron and an As—As  $d\pi$  orbital.

It has recently been observed that the main band in the spectrum of triphenylarsine is not affected when the arsine forms a 1:1 charge transfer complex with iodine (441a). A significant change would be expected if the arsenic lone pair is involved in the bonding.

### C. Other Physical Properties

In order to be able to calculate the ultraviolet spectra to be expected from arylarsines (Section III, B) it was necessary to have some idea of the ionization potential of the arsenic lone pair. Consequently the first ionization potentials of a number of simple arsines were determined and the results are given in Table V (495). The values were obtained by electron-impact mass spectrometry and may be greater than the adiabatic values, however, the trends should be reliable. The site of ionization is not known but it seems reasonable to assume that the electron is lost from the arsenic lone pair. The values also fit in well with qualitative chemical studies related to ease of complex formation and ease of solvolysis (174, 256). A value of 7.34 eV has been quoted for the first ionization potential of triphenylarsine (497). This value, determined from photoionization studies, is similar to that of a simple phenyl derivative so that the electron is probably being lost from the phenyl rings and not from the arsenic lone pair as maintained by Vilesuv and Zaitsev (497).

TABLE V

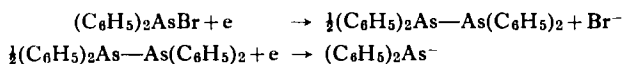
FIRST IONIZATION POTENTIALS<sup>a</sup> OF ARSINES

(CF <sub>3</sub> ) <sub>3</sub> As	11.0	(CF <sub>3</sub> ) <sub>2</sub> AsCl	11.0
(CF <sub>3</sub> ) <sub>2</sub> AsCH <sub>3</sub>	10.5	CF <sub>3</sub> AsCl <sub>2</sub>	—
CF <sub>3</sub> As(CH <sub>3</sub> ) <sub>2</sub>	9.2	AsCl <sub>3</sub>	11.7
As(CH <sub>3</sub> ) <sub>3</sub>	8.3		
		(CH <sub>3</sub> ) <sub>2</sub> AsCl	9.9
(CF <sub>3</sub> ) <sub>2</sub> AsH	10.9	CH <sub>3</sub> AsCl <sub>2</sub>	10.4
CF <sub>3</sub> AsH <sub>2</sub>	—		
AsH <sub>3</sub>	10.6 <sup>b</sup>	(CH <sub>3</sub> ) <sub>2</sub> AsH	9.0
		CH <sub>3</sub> AsH <sub>2</sub>	9.7

<sup>a</sup> Given in electron volts.<sup>b</sup> A value of 12.1 eV recently reported by Saalfeld and Svec (496) seems to be unreasonably high.

The electron-withdrawing effect of the CF<sub>3</sub> group is also seen in the order of acid strength HCl > (CF<sub>3</sub>)<sub>2</sub>AsO(OH) > CF<sub>3</sub>AsO(OH)<sub>2</sub> > CF<sub>3</sub>COOH > HNO<sub>3</sub> established by conductance measurements in acetic acid (498). The acid (CF<sub>3</sub>)<sub>2</sub>AsO(OH) is thus very much stronger than (CH<sub>3</sub>)<sub>2</sub>AsO(OH) and other alkylarsonic acids (499, 500). Even the phenylarsonic acids are fairly weak, having *K*<sub>1</sub> of the order of 10<sup>-4</sup> (501).

Polarographic data are available for a number of arsonium compounds (502), arsines and diarsines (502*a*, 502*b*). The following is a typical example of the electrolytic reduction processes encountered :



The relationship between parachor and structure of arsines has been described (503). Magnetic studies have been made on some phenyl arsenicals (504). An optical rotatory dispersion study of a spiroarsonium compound revealed that the rotation was about twice that of the corresponding phosphorus derivative (505).

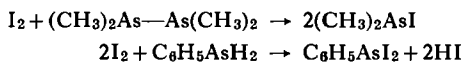
Thermochemical measurements have been made on a number of arsenic compounds. The heats of formation of trimethyl- and triphenylarsine have been used to calculate the mean dissociation energy of the As—C bonds in these compounds. The values found, 51.5 kcal/mole for the methyl compound and 60.3 kcal/mole for the other, are significantly different (506, 507).

Kinetic studies on the thermal decomposition of  $(\text{CH}_3)_3\text{As}$  and  $(\text{CF}_3)_3\text{As}$  indicate that the dissociation energy,  $D_1$ , for the process



is 54.6 kcal/mole when  $\text{R} = \text{CH}_3$  and 57.4 when  $\text{R} = \text{CF}_3$  (31). Ayscough and Emeléus also suggest that  $D_1$  for  $(\text{C}_2\text{F}_5)_3\text{As}$  is about 48 kcal/mole. The significance of these results is difficult to assess.

The heat of reaction of iodine with cacodyl and with phenylarsine has also been measured (508, 509).



Because of insufficient data the cacodyl study led only to an estimation of the As—I and As—As bond dissociation energies as 49 and 38 kcal/mole for  $(\text{CH}_3)_2\text{AsI}$  and  $(\text{CH}_3)_2\text{As}-\text{As}(\text{CH}_3)_2$ , respectively. The second investigation and related studies led to the suggestion that for the compounds  $\text{R}_n\text{AsX}_m$  ( $m+n=3$ )  $D$  values are transferable from the parent  $\text{AsX}_3$  when  $\text{R} = \text{C}_6\text{H}_5$  and  $\text{X} = \text{H}$  or  $\text{I}$ , but that enhancement can occur when  $\text{R} = \text{alkyl}$  and  $\text{X} = \text{halogen}$ , for example the 49 kcal/mole for the As—I bond in  $(\text{CH}_3)_2\text{AsI}$  mentioned above and 43 kcal/mole for the same bond in  $\text{AsI}_3$ .

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# Synthesis and Reactions of Alkylcobalt and Acylcobalt Tetracarbonyls

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This chapter reviews the methods of preparation and the chemistry of the alkylcobalt and acylcobalt tetracarbonyls. These compounds are among the most thoroughly studied of the organo-substituted transition metal carbonyl derivatives. Recent evidence suggests that the mechanisms of reaction of the various transition metal compounds are closely related. Consequently, the information obtained from the alkylcobalt and acylcobalt tetracarbonyls should provide a basis for predicting the reactions of other transition metal compounds.

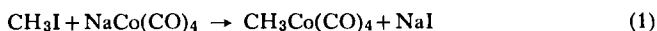
## I

### SYNTHESIS OF ALKYLCOBALT AND ACYLCOBALT TETRACARBONYLS

#### A. Alkylcobalt Tetracarbonyls

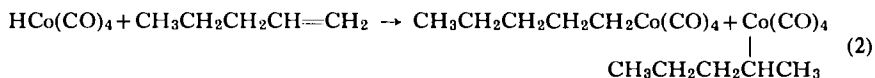
The first alkylcobalt tetracarbonyl, and indeed the first simple alkylcobalt compound of any type, was prepared by Hieber and his co-workers (20). The compound prepared, methylcobalt tetracarbonyl, was obtained in 2%

yield by the reaction of methyl iodide with sodium cobalt tetracarbonyl in ether solution. Methylcobalt tetracarbonyl is a yellow, air-sensitive solid,

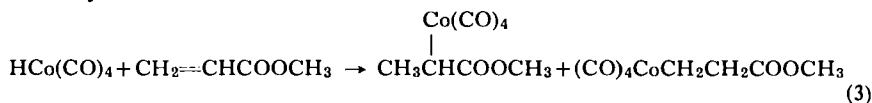


melting at  $-44^\circ\text{C}$ , and decomposing at  $-35^\circ\text{C}$ . Other alkylcobalt tetracarbonyls can be prepared by the same method (7). Often, however, the rates of formation and decomposition of the alkylcobalt tetracarbonyls approach each other and the yields are poor. If the alkylcobalt tetracarbonyl is being prepared to be used in another reaction, the other reaction can usually be carried out simultaneously with the formation step so that the alkylcobalt tetracarbonyl reacts before it decomposes. High yields are often obtained in these combined reactions. The alkylcobalt tetracarbonyls are also obtained by the reaction of dialkyl sulfates, alkyl sulfonates, and trialkyl oxonium salts with sodium cobalt tetracarbonyl (4, 8).

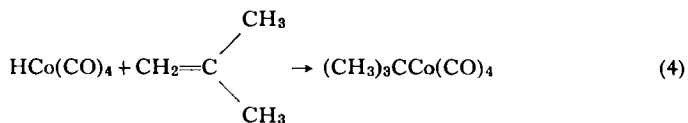
A second method for preparing alkylcobalt tetracarbonyls involves the addition of cobalt hydrocarbonyl to olefins (5). With unsymmetrical olefins, two isomeric alkylcobalt tetracarbonyls are possible, depending upon the direction of addition of the cobalt hydrocarbonyl. Both possible isomers are often obtained. 1-Pentene and cobalt hydrocarbonyl at  $0^\circ\text{C}$  give a 50:50 mixture of the two possible pentylcobalt tetracarbonyls. Methyl acrylate



and cobalt hydrocarbonyl give a 5:1 mixture of the  $\alpha$ - and  $\beta$ -cobalt tetracarbonyl isomers.



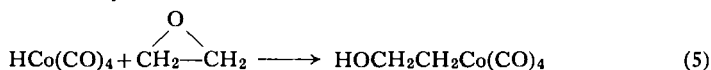
Isobutylene and cobalt hydrocarbonyl at  $0^\circ\text{C}$ , on the other hand, give entirely one isomer, *tert*-butylcobalt tetracarbonyl.



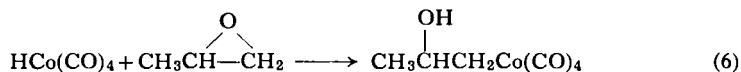
Besides the expected isomers from unsymmetrical olefins, "unexpected" ones also may be produced. Cobalt hydrocarbonyl has been shown to isomerize olefins rapidly (3) and, of course, addition of cobalt hydrocarbonyl

to the isomerized olefins would give "unexpected" alkylcobalt tetracarbonyls. There is also evidence that, once formed, alkylcobalt tetracarbonyls may isomerize relatively slowly intramolecularly (29).

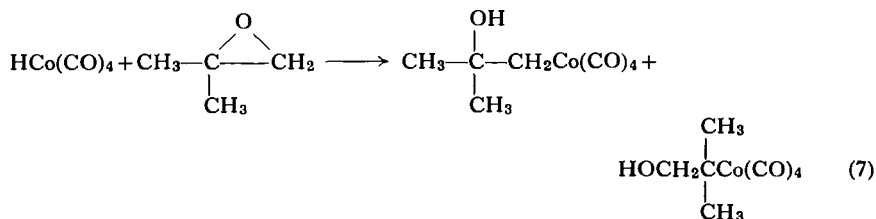
A third method for preparing alkylcobalt tetracarbonyls is the reaction of cobalt hydrocarbonyl with epoxides. The products are 2-hydroxyalkylcobalt tetracarbonyl derivatives (9). Ethylene oxide produces 2-hydroxyethylcobalt tetracarbonyl.



Propylene oxide gives 2-hydroxypropylcobalt tetracarbonyl.

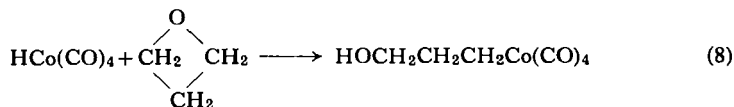


Cyclohexene oxide yields entirely *trans*-2-hydroxycyclohexylcobalt tetracarbonyl. Isobutylene oxide produces a mixture of products, 93% of 2-hydroxy-2-methylpropyl- and 7% of 1,1-dimethyl-2-hydroxyethylcobalt tetracarbonyl.



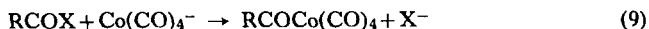
In this last example, the electronic effects are apparently approaching the importance of the steric effects.

Trimethylene oxide reacts similarly with cobalt hydrocarbonyl producing 3-hydroxypropylcobalt tetracarbonyl (9).

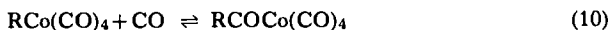


## B. Acylcobalt Tetracarbonyls

Two general methods are available for the synthesis of acylcobalt tetracarbonyls. One method is the reaction of acyl halides with salts of cobalt hydrocarbonyl (7). This reaction is applicable to all types of acid halides,



even hindered ones such as pivalyl and mesityl chlorides. The other method of synthesis of acylcobalt tetracarbonyls is the reaction of alkylcobalt tetracarbonyls with carbon monoxide (7). This is a reversible reaction but the



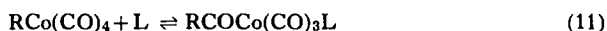
equilibrium is usually far on the side of the acylcobalt tetracarbonyl at or below room temperature and under 1 atm or more of carbon monoxide. The acylcobalt tetracarbonyls are generally more stable than are the alkylcobalt tetracarbonyls.

## II

### REACTIONS OF ALKYLCOBALT AND ACYLCOBALT TETRACARBONYLS

#### A. Ligand Replacement Reactions

The coordinated carbonyl groups of the alkylcobalt and acylcobalt tetracarbonyls may be replaced by other ligands. When alkylcobalt tetracarbonyls react with ligands, they generally form acylcobalt tricarbonyl derivatives.



The formation of acylcobalt tetracarbonyls from alkylcobalt tetracarbonyls and carbon monoxide described above is an example of this type of reaction. The similar reactions with triarylphosphines and phosphite esters have been thoroughly studied because the equilibria are far on the side of the acyl compounds and the products are convenient derivatives to prepare from the alkylcobalt tetracarbonyls (7, 10). The triarylphosphine and phosphite ester derivatives are much more thermally and oxidatively stable than the alkylcobalt tetracarbonyls themselves.

The acylcobalt tetracarbonyls react with ligands by losing carbon monoxide, producing the same acylcobalt tricarbonyl derivatives as obtained from the alkylcobalt tetracarbonyls and the same ligands (7).

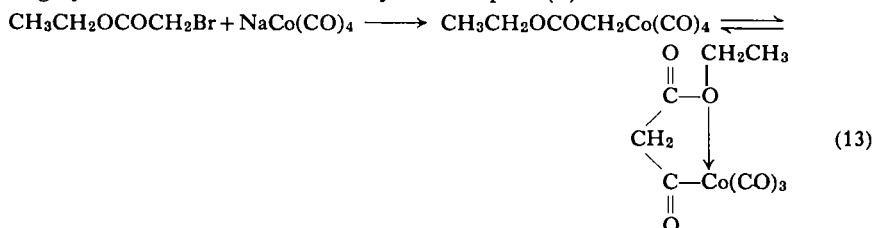


#### 1. Replacements by Internal Ligands Forming Chelates

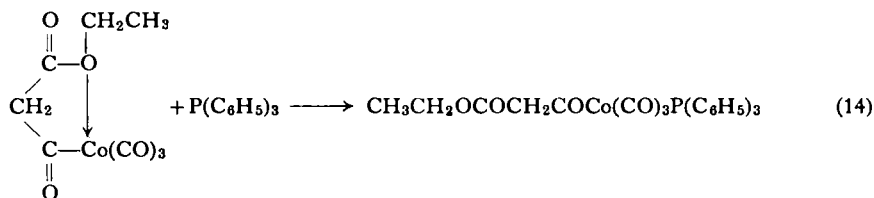
Several examples have been found in which the reacting ligand is attached to the alkyl or acyl group of the alkylcobalt or acylcobalt carbonyl complex



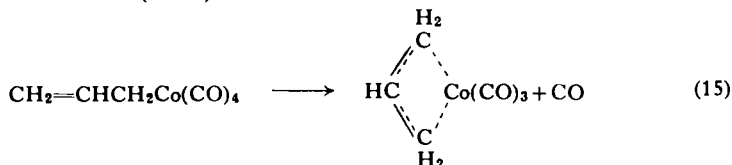
so that cyclic, chelated products are formed. Carbomethoxycobalt tetracarbonyl, for example, prepared from ethyl bromoacetate and sodium cobalt tetracarbonyl, appears to exist, under 1 atm of carbon monoxide at 0°C, largely as an ester-coordinated cyclic complex (7).



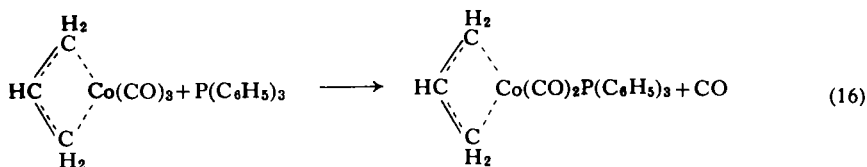
The product reacts with triphenylphosphine to produce the open-chain derivative.



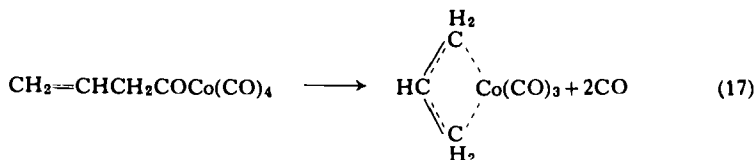
Allylic cobalt tetracarbonyls are less stable than saturated alkylcobalt tetracarbonyls because they very readily evolve carbon monoxide and form  $\pi$ -allylcobalt tricarbonyls. Nuclear magnetic resonance studies have shown that these  $\pi$ -allylcobalt complexes possess symmetrical rather than unsymmetrical structures (6, 25).



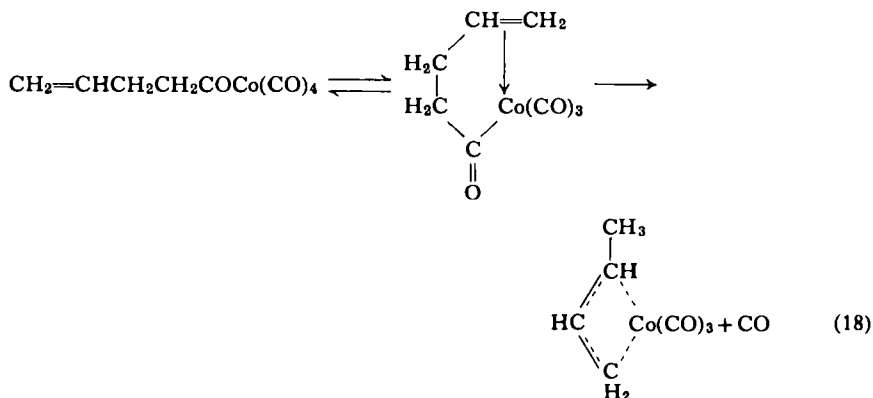
The  $\pi$ -allylcobalt tricarbonyls are relatively stable organocobalt compounds. Most are stable at room temperature or above. Triphenylphosphine reacts with  $\pi$ -allylcobalt tricarbonyl by replacing a coordinated carbonyl group rather than by opening the  $\pi$ -allyl ring (6).



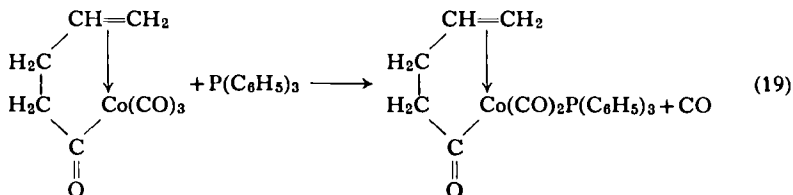
There is a strong tendency for unsaturated alkylcobalt and acylcobalt tetracarbonyls to form  $\pi$ -allyl complexes. 3-Butenylcobalt tetracarbonyl rapidly loses 2 moles of carbon monoxide at room temperature, forming  $\pi$ -allylcobalt tricarbonyl in high yield (6).



Even 4-pentenylcobalt tetracarbonyl, which exists at 0° C under 1 atm of carbon monoxide entirely as the cyclic  $\pi$  complex, decomposes into 1-methyl- $\pi$ -allylcobalt tricarbonyl when heated to 35° C (6).



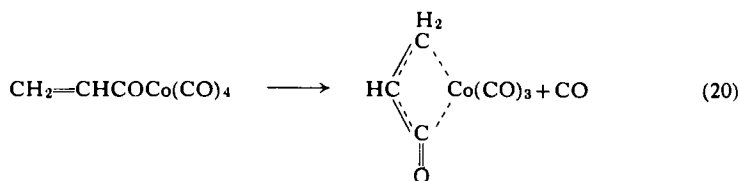
$\pi$ -4-Pentenylcobalt tricarbonyl reacts with triphenylphosphine by replacing a coordinated carbonyl group rather than the coordinated double bond (6).



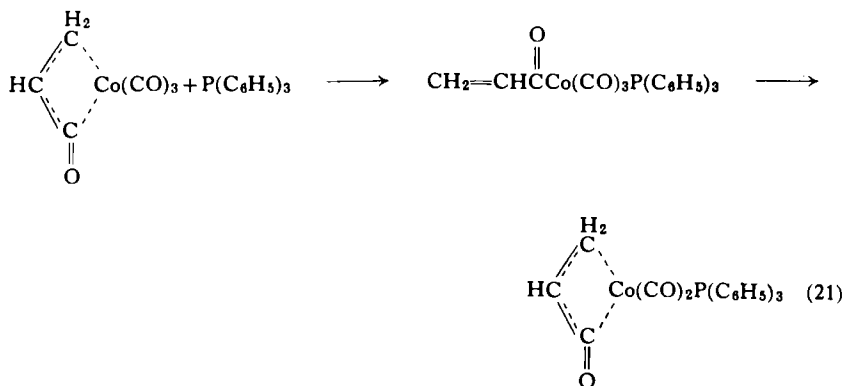
5-Hexenylcobalt tetracarbonyl does not form a chelated  $\pi$  complex at 0° C under 1 atm of carbon monoxide (11).

Chelated  $\pi$ -olefin complexes are also formed from  $\alpha,\beta$ -unsaturated acylcobalt tetracarbonyls. Acrylylcobalt carbonyl exists, at least mainly, as

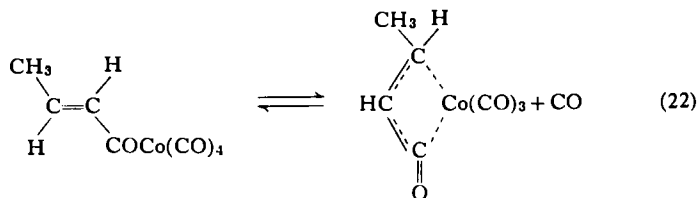
the  $\pi$ -acrylylcobalt tricarbonyl at 0° C and under 1 atm of carbon monoxide (6).



The  $\pi$ -acrylylcobalt tricarbonyl reverts to the simple  $\sigma$ -bonded derivative when it is treated with triphenylphosphine at 0° C. The  $\pi$ -acrylyl system is reformed when the  $\sigma$  complex is isolated at room temperature.

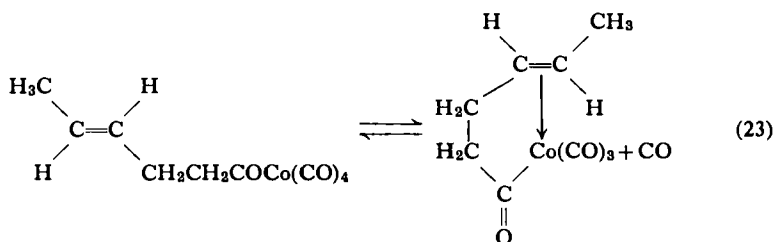


Thus, the three-carbon and the five-carbon chelated  $\pi$  complexes of cobalt are more stable than the four- or six-carbon or probably larger ring complexes. Substituents on the coordinating olefinic group affect the stability of the cyclic complexes. *trans*-Methyl groups decrease the relative stability of the cyclic structures. Crotonylcobalt carbonyl, at 0° C under 1 atm of carbon monoxide, exists as an equilibrium mixture containing 56% of the open-chain complex and 44% of the cyclic  $\pi$  complex.



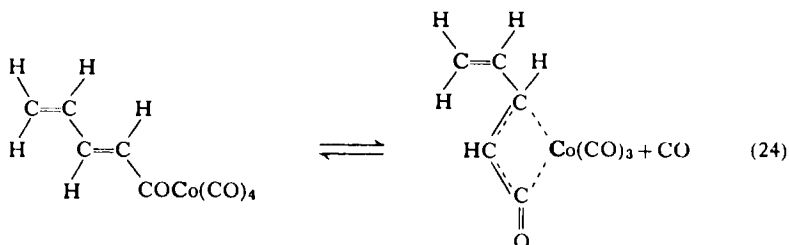
Triphenylphosphine converts both compounds into crotonyl(triphenylphosphine)cobalt tricarbonyl (12). *trans*-4-Hexenoylcobalt carbonyl under

the same conditions consists of an equilibrium mixture containing 52% of the open-chain derivative and 48% of the cyclic one.



Again triphenylphosphine forms the open-chain derivative from both forms (11).

Conjugated dienoylcobalt carbonyls form cyclic  $\pi$  complexes also (13). *trans*-2,4-Pentadienoylcobalt carbonyl at 0°C, under 1 atm of carbon monoxide, exists as an equilibrium mixture containing 64% of the open-chain compound and 36% of a cyclic  $\pi$  complex, which is, at least mainly, the 2,3- $\pi$  complex rather than the 4,5-complex.



*trans*-2,4-Hexadienoylcobalt carbonyl, under the same conditions, exists as a mixture of 80% of the open-chain form and 20% of the cyclic form. Both forms of the pentadienyl- and hexadienoylcobalt carbonyls form the open-chain derivatives with triphenylphosphine at room temperature (11).

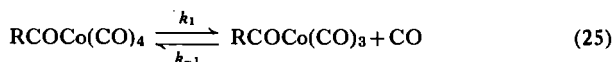
Chelation in acylcobalt carbonyls is surely possible by groups other than esters and olefins, but other examples have not been reported.

## 2. Replacements by External Ligands

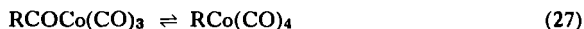
Ethers, esters, alcohols, ketones, water, amines, arsines, stibines, and phosphorus trichloride displace carbon monoxide only partially or not at all from acetylcobalt tetracarbonyl under 1 atm of carbon monoxide at 0°C or 25°C. Arylphosphines and phosphite esters, on the other hand, react

essentially completely under the same conditions, forming monophosphine or phosphite derivatives.

Kinetic measurements have shown that the reaction of acylcobalt tetracarbonyls with triphenylphosphine is first order in the cobalt compound and zero order in the triphenylphosphine down to at least 0.02 *M* (12). A first-order dissociation of the acylcobalt tetracarbonyl into an acylcobalt tricarbonyl and carbon monoxide has been proposed as the rate-determining step to explain the kinetics. The fast second step of the mechanism is then the reaction of the acylcobalt tricarbonyl with the triphenylphosphine, forming the acyl(triphenylphosphine)cobalt tricarbonyl.



The intermediate acylcobalt tricarbonyl is very probably also in equilibrium with the corresponding alkylcobalt tetracarbonyl and this equilibrium would explain why the acylcobalt and alkylcobalt tetracarbonyls react so similarly.



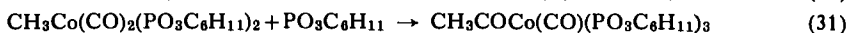
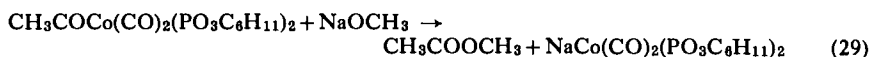
Under the conditions used for the kinetic measurements  $k_{-1}[\text{RCOCo(CO)}_3]$  and  $k_{-2}[\text{RCOCo(CO)}_3\text{P(C}_6\text{H}_5)_3]$  are negligibly small and the rate constant measured is essentially just  $k_1$ , the rate of dissociation of the acylcobalt tetracarbonyl.

Measurement of dissociation rates of several different acylcobalt tetracarbonyls has yielded useful information about steric and electronic effects in the dissociation reaction (12). Increasing the size of the acyl group from acetyl- to isobutyryl- to pivalylcobalt tetracarbonyl increased the relative rates of dissociation from 1.0 to 2.1 to 86. Even though cobalt is a fairly large atom, steric effects do appear in these pentacoordinated complexes. Loss of a coordinated carbonyl group seems to reduce the steric interaction between the other coordinated groups. Increasing the electron-withdrawing ability of the acyl group decreases the rate of dissociation. The relative rates of dissociation of acetyl-, methoxyacetyl-, and trifluoroacetylcobalt tetracarbonyl are 1.0 to 0.3 to 0.1. Since cobalt loses a shared pair of electrons when dissociation takes place, the bonding of electron-withdrawing groups to the cobalt would reasonably be expected to make dissociation more difficult.

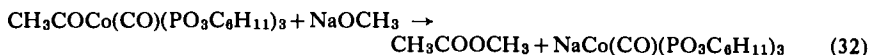
Under no conditions has it been found possible to replace more than one carbonyl group of acetylcobalt tetracarbonyl by triphenylphosphine. Even the chelating bis(phosphine), ethylenebis(diphenylphosphine) does not form stable chelated complexes with acetylcobalt tetracarbonyl (7). Phosphite esters, on the other hand, will replace two coordinated carbonyl groups at about 80° C, and three can be replaced by another method (8).



Acylcobalt carbonyl derivatives are cleaved by sodium methoxide to esters and sodium salts of the corresponding carbonyl anions. By means of this reaction, acetyl[bis(trimethylolpropane phosphite)]cobalt dicarbonyl has been converted into sodium [bis(trimethylolpropane phosphite)]cobalt dicarbonyl. The latter compound is readily alkylated by methyl iodide to form the methylcobalt derivative and this compound in turn reacts with another mole of the phosphite ester, in the same way that methylcobalt tetracarbonyl does, to form acetyl[tris(trimethylolpropane phosphite)]cobalt carbonyl:

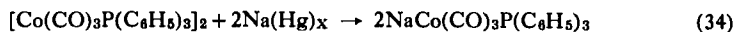


This sequence of reactions may be carried further by cleaving the last product with sodium methoxide and alkylating again with methyl iodide to produce methyl[tris(trimethylolpropane phosphite)]cobalt:



The latter compound does not react further with more phosphite ester (10).

Mixed phosphite ester-phosphine coordinated acylcobalt carbonyl derivatives have also been prepared. Methyl(triphenylphosphine)cobalt tricarbonyl, which cannot be produced by a simple ligand replacement reaction, can be obtained by another method. Hieber and Lindner (21) found that bis(triphenylphosphine)dicobalt hexacarbonyl reacts with sodium amalgam to form sodium(triphenylphosphine)cobalt tricarbonyl and that this compound reacted with methyl iodide to form methyl-(triphenylphosphine)cobalt tricarbonyl.



The last-mentioned compound does not react further with triphenylphosphine, but it does with trimethyl phosphite, forming acetyl(trimethyl phosphite)(triphenylphosphine)cobalt dicarbonyl (10).



With a large excess of trimethyl phosphite, the triphenylphosphine is replaced, forming acetyl[bis(trimethyl phosphite)]cobalt dicarbonyl. The bis- and tris(phosphite) derivatives of acetylcobalt tetracarbonyl are more thermally stable and more resistant to air oxidation than are the monophosphite or triphenylphosphine derivatives.

## B. Carbon-Cobalt Cleavage Reactions

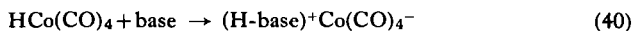
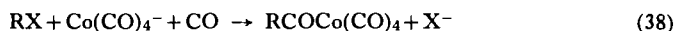
### 1. Alcoholysis and Ammonolysis

Acylcobalt tetracarbonyls react slowly with alcohols at room temperature, more rapidly at elevated temperatures, to form esters and cobalt hydrocarbonyl (8).



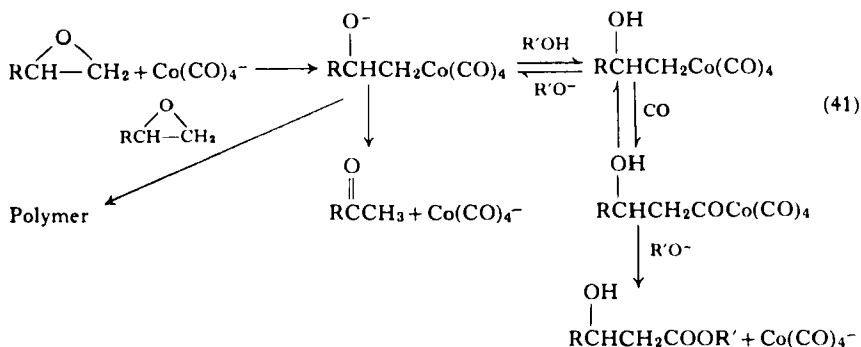
The reaction is catalyzed by bases but not by acids. The reaction appears to involve a simple attack of alcohol or alkoxide ion upon the carbonyl group of the acylcobalt tetracarbonyl.

If the alcoholysis reaction is carried out in the presence of base, the acidic cobalt hydrocarbonyl is converted into a salt. This base-catalyzed reaction has been used as the basis for a catalytic, one-step alkoxycarbonylation of alkyl halides with carbon monoxide and an alcohol (8).



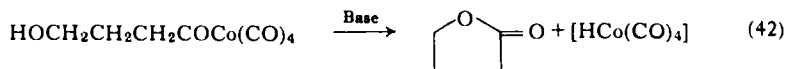
This alkoxycarbonylation reaction is also catalytic, if the alkylcobalt tetracarbonyl is formed from an epoxide and cobalt carbonyl anion in a hydroxylic solvent (9). A stoichiometric amount of base is not required in this reaction. The initial product, a derivative of the anion of 2-hydroxyethylcobalt tetracarbonyl, may undergo three reactions: (a) react with more epoxide to give polymer, (b) undergo an internal hydride shift to form aldehyde or ketone, or (c) undergo protonation, carbon monoxide insertion, and alcoholysis (or hydrolysis) to form ester (or acid). Varying amounts of

the three types of products are formed depending upon the epoxide used and the reaction conditions.



In spite of relatively low yields, this reaction offers a convenient and useful synthetic procedure for preparing esters of  $\beta$ -hydroxy acids.

The alcoholysis reactions can take place internally if there is a hydroxyl group in the 4- or 5-position of the acyl chain in the acylcobalt tetracarbonyl. 4-Hydroxybutyrylcobalt tetracarbonyl, for example, reacts with itself in the presence of a base to form butyrolactone and cobalt carbonyl anion (9).



Primary and secondary amines also cleave acylcobalt tetracarbonyls under mild conditions, producing amides and amine salts of cobalt hydrocarbonyl (8).



## 2. Reductive Cleavages

Two reducing agents which cleave acylcobalt carbonyls are known: hydrogen and cobalt hydrocarbonyl.

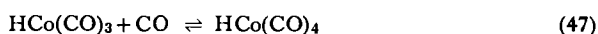
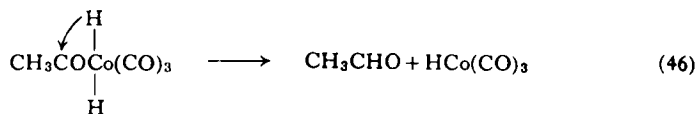
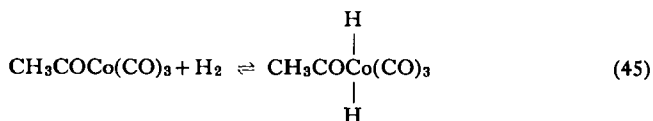
Hydrogen at room temperature and under high pressure (3000 psi) rapidly reduces acetylcobalt tetracarbonyl to acetaldehyde and cobalt hydrocarbonyl (4).



That cobalt hydrocarbonyl is not involved in the reduction was shown by the fact that the reduction proceeded just as well in the presence of a strongly basic, hindered amine, dicyclohexylethylamine, which converts the cobalt hydrocarbonyl into an inert, insoluble salt. This reduction reaction is

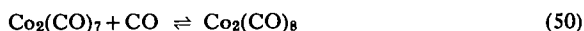
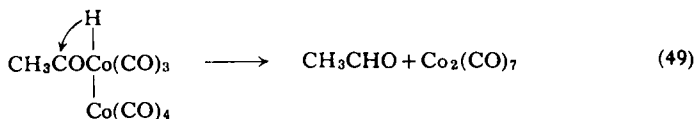
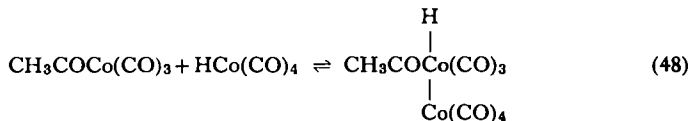


strongly inhibited by carbon monoxide, suggesting that it is not the acetyl-cobalt tetracarbonyl itself that is reacting but rather the dissociated compound, acetylcobalt tricarbonyl. By analogy with the reaction of an iridium(I) compound (30), the assumption is reasonable that hydrogen and the acetyl-cobalt tricarbonyl first form a cobalt(III) dihydride (23) and that this complex then undergoes a 1:2 shift of a hydride group from cobalt to carbon, forming acetaldehyde and cobalt hydrotricarbonyl. The hydrotricarbonyl then reacts with the carbon monoxide formed in the dissociation step and produces cobalt hydrotetracarbonyl.



This reduction is very likely the last step in the industrially important hydroformylation or oxo reaction for converting olefins into aldehydes (4). The catalytic species seems to be cobalt hydrocarbonyl, which first adds to the olefin as in Eq. (2). The alkylcobalt tetracarbonyl so formed then probably isomerizes to the acylcobalt tricarbonyl [Eq. (25)] and is reduced by hydrogen as in Eqs. (45) and (46).

Cobalt hydrocarbonyl also readily reduces acylcobalt tetracarbonyls, producing aldehydes and cobalt octacarbonyl (4). In this reaction, as in the hydrogen reduction, carbon monoxide is an inhibitor. The reaction probably involves the addition of cobalt hydrocarbonyl to an acylcobalt tricarbonyl followed by a hydride shift from cobalt to carbon, producing aldehyde and dicobalt heptacarbonyl.



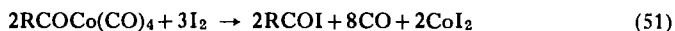
There is other evidence to support the suggestion that  $\text{Co}_2(\text{CO})_7$  does exist. The formation of cobalt hydrocarbonyl from dicobalt octacarbonyl and hydrogen is strongly inhibited by carbon monoxide (26). This fact again suggests that a coordinately unsaturated carbonyl is an intermediate, and  $\text{Co}_2(\text{CO})_7$  would seem to be the most likely one.

### 3. *Oxidative Cleavages*

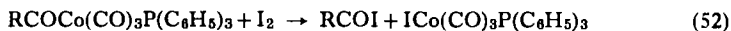
Alkylcobalt and acylcobalt tetracarbonyls are generally rapidly oxidized by air but the products of this reaction have not been investigated. Presumably the products are carboxylic acids and cobalt oxide.

Halogens have been widely used in organometallic chemistry as oxidizing agents. Iodine oxidations have been particularly useful in cobalt carbonyl chemistry because the reaction usually liberates all of the coordinated carbon monoxide in the complex quantitatively. This reaction makes possible analyses of even the most unstable organocobalt carbonyl derivatives. The ratio of coordinated carbon monoxide to cobalt is readily determined by measuring the volume of gas evolved during the reaction and the concentration of cobalt remaining in the solution after the reaction is complete (28, 4).

Organic groups in organocobalt complexes are usually cleanly cleaved by iodine. Acylcobalt tetracarbonyls give acyl iodides, apparently in high yield (5).



The mechanism of this reaction was investigated to find out if carbon monoxide dissociation is the rate-determining step (16). The rate of the reaction of acetylcobalt tetracarbonyl with iodine is too fast to measure under conditions which allow dissociation rate to be measured easily. Thus, dissociation is not rate-determining, and the acylcobalt tetracarbonyl and the iodine must be reacting directly. Further studies with the less reactive acyl(triphenylphosphine)cobalt tricarbonyls showed that the first step in the reaction with iodine is a rapid cleavage of the cobalt-carbon bond to form acyl iodide and iodo(triphenylphosphine)cobalt tricarbonyl.

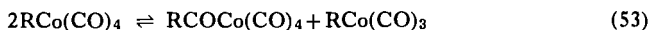


This reaction is the most convenient method now available for preparing the iodocobalt complex. The further reaction of iodo(triphenylphosphine)-cobalt tricarbonyl with iodine appears to be first order in the cobalt complex

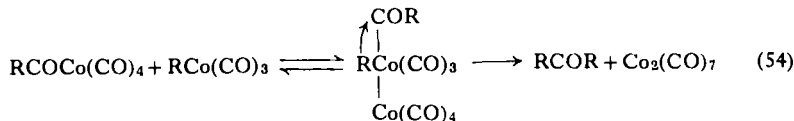
and zero order in iodine. Excess iodine is necessary in this reaction because the reaction products complex with iodine. Therefore, it has not been possible to distinguish between two likely mechanisms for the final part of the iodine reaction. The two possibilities are: (a) carbon monoxide dissociation is rate-determining or (b) decomposition of a rapidly formed, relatively stable complex between iodine and the iodocobalt tricarbonyl triphenylphosphine is rate-determining. The latter possibility seems more probable in view of the fact that other oxidizing agents, bromine and *tert*-butyl hypochlorite, oxidize iodo(triphenylphosphine)cobalt tricarbonyl faster than iodine does. The same rates would be expected if all involved dissociation as the slow step in the reactions.

#### 4. Thermal Decomposition

The alkylcobalt tetracarbonyls decompose fairly rapidly at 0° C even in dilute solution. One of the decomposition products seems to be the corresponding acylcobalt tetracarbonyl (22). This product was first thought to be the isomeric form of the alkylcobalt tetracarbonyl, the acylcobalt tricarbonyl (4, 10, 22). The formation of acylcobalt tetracarbonyls from alkylcobalt tetracarbonyls probably involves a disproportionation reaction forming, at least as a transitory intermediate, an alkylcobalt tricarbonyl.



Warming pure alkylcobalt tetracarbonyls, or their solutions, to room temperature or above causes a further reaction to take place, producing dialkyl ketones (1). These products can be accounted for by assuming that the acylcobalt tetracarbonyl adds to the alkylcobalt tricarbonyl as cobalt hydrocarbonyl probably adds to an acylcobalt tricarbonyl [Eq. (48)]. The cobalt(III) intermediate could then decompose and form ketone and a mixture of cobalt carbonyls.



Addition-elimination reactions of this type are probably much more common in organometallic chemistry than is now generally believed.

### C. Insertion Reactions

Reactions in this group involve the insertion of a compound with an available pair of electrons,  $L:$  (not necessarily unshared electrons), between the alkyl or acyl carbon atom and the cobalt atom of an alkylcobalt or acylcobalt tetracarbonyl (18).



The term "insertion reaction" is used only to indicate the type of product formed and does not imply any specific mechanism for the reaction. The initial insertion products are generally not the final ones formed in the reactions; disproportionations or internal ligand replacements are often involved in the final steps.

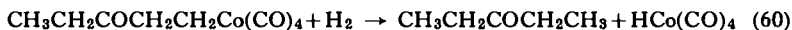
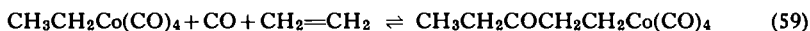
#### 1. Insertion Reactions of Carbon Monoxide

The one example where the simple insertion product is a stable product is the carbon monoxide insertion reaction. The addition of carbon monoxide to alkylcobalt tetracarbonyls to form acylcobalt tetracarbonyls has already been discussed above because of its basic importance in alkylcobalt and acylcobalt carbonyl chemistry. The mechanism of this insertion is thought to involve a 1:2 shift of the alkyl group from cobalt to carbon followed by reaction of the intermediate acylcobalt tricarbonyl with another external carbon monoxide. Although there is no conclusive evidence for or against this mechanism in the carbonylation of cobalt compounds, there is evidence for it in the related carbonylation of alkylmanganese pentacarbonyls (2, 24).

#### 2. Insertion Reactions of Olefins

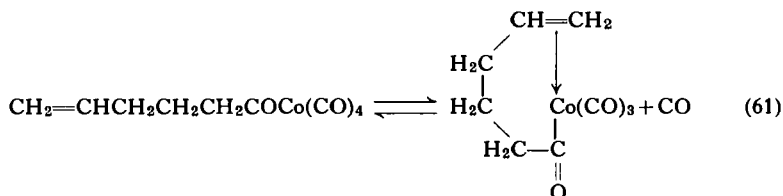
The formation of diethyl ketone from ethylene, carbon monoxide, and a limited amount of hydrogen, with a cobalt catalyst (27), can be explained on the basis of an olefin insertion reaction (11). Propionylcobalt tetracarbonyl would be formed from the cobalt catalyst, carbon monoxide, ethylene, and hydrogen. An insertion reaction of propionylcobalt tetracarbonyl with ethylene would form 2-propionylethylcobalt tetracarbonyl. The latter compound could then be reduced by hydrogen to ketone and cobalt hydrocarbonyl.  $\beta$ -Acylethylcobalt tetracarbonyl derivatives are thought to be extremely reactive because several attempts to prepare them have failed (11). In the presence of reducing agents, they appear to decompose into saturated carbonyl compounds, while, in the absence of reducing agents, disproportionation seems to take place, giving saturated and unsaturated ketones.

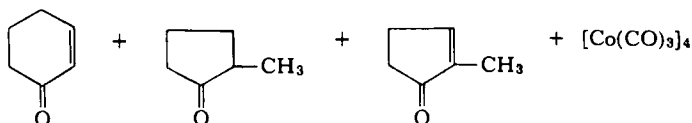
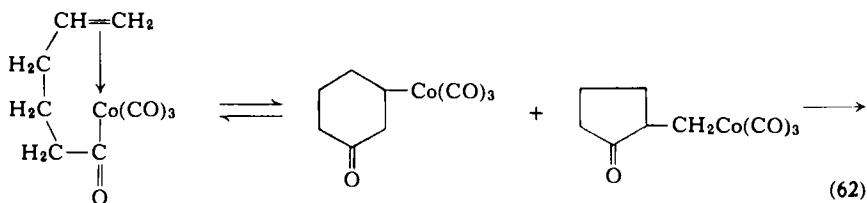
Thus the diethyl ketone synthesis may be explained by the following equations:



By analogy with other insertion reactions, coordinately unsaturated intermediates are probably the true reactants in Eqs. (58), (59), and (60).

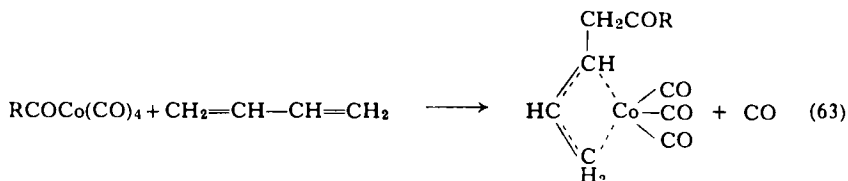
This proposed mechanism receives support from experiments carried out with 5-hexenoylcobalt tetracarbonyl (11). This compound, prepared from 5-hexenoyl chloride and sodium cobalt tetracarbonyl, exists at 0° C under 1 atm of carbon monoxide essentially entirely as the open-chain derivative rather than cyclic olefin  $\pi$  complex. On warming to 25° C, this complex undergoes a spontaneous reaction, forming a mixture of cyclic ketones and cobalt tri- and octacarbonyl. The ketone mixture contained 54% of 2-methylcyclopentanone, 16% of 2-methylcyclopentenone, and 8% of cyclohexenone. This reaction is easily explained as an internal olefin insertion reaction followed by a disproportionation. Part of the unsaturated ketone product was apparently lost, probably by polymerization. The initial step of this reaction would reasonably be expected to be the formation of the cyclic  $\pi$ -olefin complex, since the 4-pentenoylcobalt carbonyl does this so easily. The geometry in the 4-pentenoyl compound is apparently not favorable for the double bond to react with the cobalt-carbon system, but the longer 5-hexenoyl group can reach around and react with itself. Insertion, with prior formation of a  $\pi$  complex is analogous to the insertion of the coordinated carbonyl group in methylmanganese pentacarbonyl mentioned above. There is no evidence other than this analogy, however, to suggest that the  $\pi$  complex is a true intermediate. The reaction is written here as involving this intermediate, but with the present evidence it could just as well be written as a simple four-centered addition reaction.





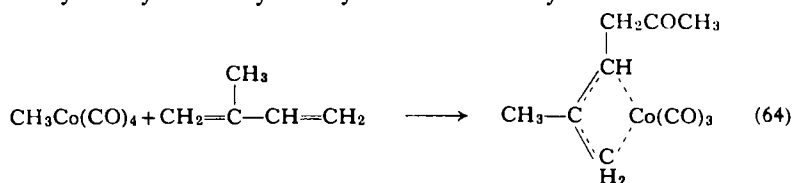
### 3. Insertion Reactions of Conjugated Dienes

Acylcobalt tetracarbonyls add to conjugated dienes to produce 1-acylmethyl- $\pi$ -allylcobalt tricarbonyls and carbon monoxide (14).

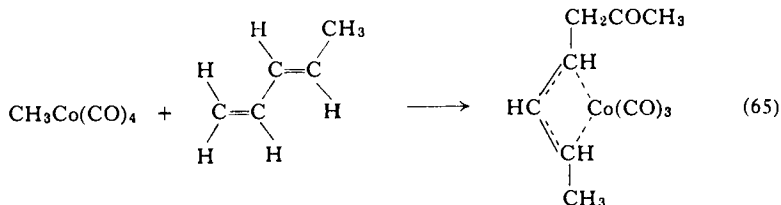


The same reaction occurs much more rapidly and without gas evolution with alkylcobalt tetracarbonyls and conjugated dienes (14). Thus, the reaction probably involves the addition of an acylcobalt tricarbonyl to the diene, perhaps by way of a  $\pi$  complex, either 1:2 or 1:4 and then a cyclization to the  $\pi$ -allyl derivative.

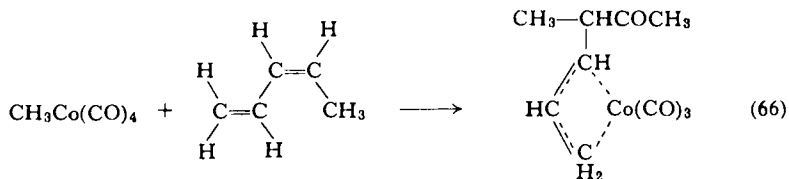
The addition of acylcobalt carbonyls to conjugated dienes is a very general reaction (14, 15). Some information on the reactivity of differently substituted double bonds in the diene system can be obtained from the structures of the 1-acylmethyl- $\pi$ -allylcobalt tricarbonyls formed from them. The acyl group is reasonably assumed to add to the least-hindered and most reactive double bond. Isoprene reacts with methylcobalt tetracarbonyl to form 1-acetylmethyl-2-methyl- $\pi$ -allylcobalt tricarbonyl.



Thus, the monosubstituted double bond is more reactive than the disubstituted. *trans*-Piperylene and methylcobalt tetracarbonyl form 1-acetylmethyl-4-methyl- $\pi$ -allylcobalt tricarbonyl.

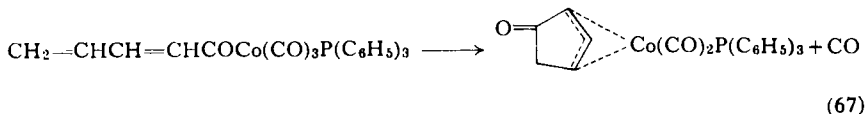


*cis*-Piperylene on the other hand, reacts the other way, producing 1-(1-acetylethyl)- $\pi$ -allylcobalt tricarbonyl.

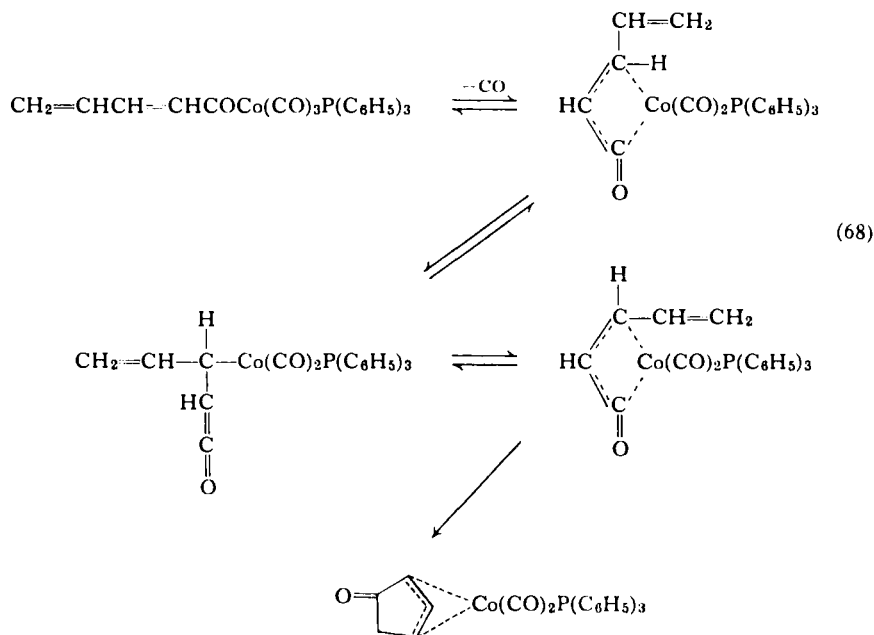


It seems that the *cis* double bond is more reactive than the terminal double bond and that the terminal double bond is more reactive than the *trans* double bond.

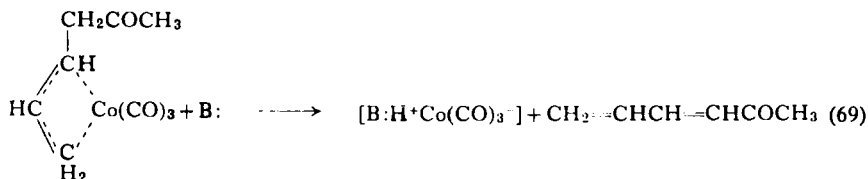
The diene insertion reaction will take place intramolecularly if the diene system is part of the acyl group in the acylcobalt tetracarbonyl (13). Thus, *trans*-2,4-pentadienyl(triphenylphosphine)cobalt tricarbonyl, prepared by the acid chloride method, cyclizes on heating in ether solution in a closed vessel at 75° C for an hour, to  $\pi$ -cyclopentenyl(triphenylphosphine)cobalt dicarbonyl in 30% yield.



The yield is low, probably because the starting material must be isomerized from a *trans* to a "*cis* compound" in the reaction before cyclization can occur. One way that this isomerization might occur is for the  $\pi$ -propenone compound, which is very likely present in the reaction mixture in equilibrium with the starting compound, to open to a  $\sigma$ -bonded ketene derivative and reclose as the other isomer. This can then cyclize as shown in Eq. (68).



The 1-acylmethyl- $\pi$ -allylcobalt tricarbonyl complexes react with bases to eliminate the elements of cobalt hydrotricarbonyl and form acyldienes (15).

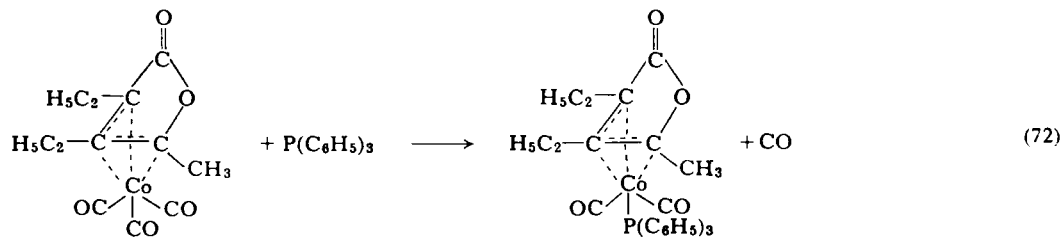
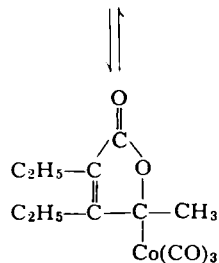
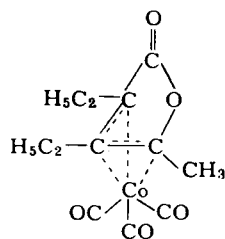
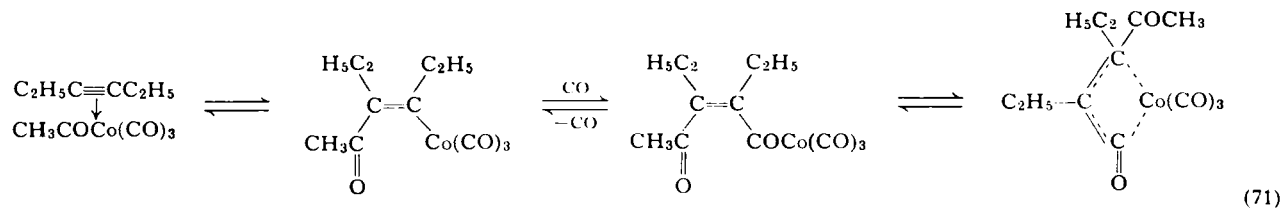
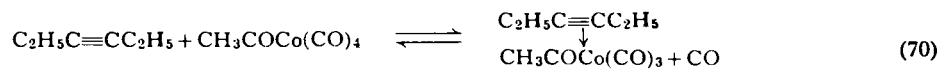


This reaction can be carried out catalytically with respect to cobalt carbonyl anion, if the 1-acylmethyl- $\pi$ -allylcobalt tricarbonyl is prepared *in situ* from an alkyl or acyl halide, cobalt carbonyl anion, and a diene under carbon monoxide. This method is perhaps the most versatile and generally useful method now available for the preparation of acyldienes.

#### 4. Insertion Reactions of Acetylenes

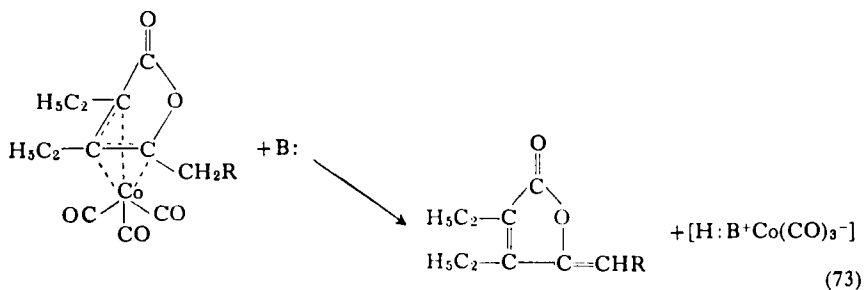
Acetylenes readily undergo insertion reactions with alkylcobalt and acylcobalt tetracarbonyls (17). Complicated mixtures of products are obtained from acetylene itself and monosubstituted acetylenes. A pure





product has been isolated from the reaction of acetylcobalt tetracarbonyl with 3-hexyne. The reaction, at 0° C, evolved a mole of carbon monoxide, and a new cobalt complex was isolated as its monotriphenylphosphine derivative. The initial product was shown to be 2,3-diethyl- $\pi$ -(2,4)-(penteno-4-lactonyl)cobalt tricarbonyl. The mechanism of the insertion step seems to be analogous to the other insertion reactions. The insertion product, an acylacrylylcobalt tricarbonyl, then probably cyclizes by adding its cobalt-acyl group to the ketonic carbonyl, forming a lactone which then coordinates, producing a  $\pi$ -allylcobalt complex.

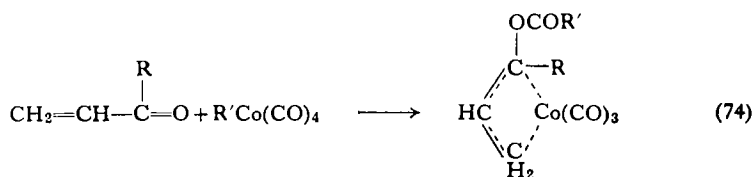
Proton-activating groups such as nitrile, ester, or *p*-nitrophenyl, on carbon atom 5 of the  $\pi$ -(penteno-4-lactonyl)cobalt tricarbonyl complexes make the compounds reactive toward bases. Bases cause the elimination of cobalt tricarbonyl anion and 5-substituted 2,4-pentadieno-4-lactones are produced (17).



Acetylene and monosubstituted acetylenes appear to give some of the  $\pi$ -(penteno-4-lactonyl)cobalt tricarbonyl complexes on reaction with alkylcobalt or acylcobalt tetracarbonyls also but other products are formed too. These other products have not been characterized but are thought to be linear, low molecular weight polymers of the acetylene or of the acetylene and carbon monoxide with an acyl group at one end of the polymer chain and a cobalt carbonyl group at the other. The formation of cyclic products from the more-substituted compounds and cyclic and linear ones from the less-substituted compounds is explainable because substitution is known to improve many cyclization reactions.

### 5. Insertion Reactions of Carbonyl Compounds

Insertion reactions of alkylcobalt or acylcobalt tetracarbonyls with saturated aldehydes or ketones have not been observed. Carbonyl insertions do occur in some unsaturated carbonyl systems, however. The cyclization of the intermediate acylacrylylcobalt tricarbonyls, formed from acetylenes and alkylcobalt or acylcobalt tetracarbonyls, to butenolactone derivatives, as described above, is one example of the reaction. Another example is the addition of alkylcobalt or acylcobalt tetracarbonyls to  $\alpha,\beta$ -unsaturated aldehydes or ketones. In this reaction an acyl group from the cobalt compound is added to a carbonyl oxygen and the cobalt carbonyl group forms a  $\pi$ -allyl system with the carbonyl carbon and the double bond (19).



## III

### SUMMARY

Alkylcobalt tetracarbonyls are readily obtainable from the reaction of alkylating agents with cobalt carbonyl anion or from cobalt hydrocarbonyl and olefins or epoxides. Acylcobalt tetracarbonyls are produced by reacting alkylcobalt tetracarbonyls with carbon monoxide or by reacting acyl halides with cobalt carbonyl anion. The very reactive alkylcobalt and acylcobalt tetracarbonyls produce the same products in most reactions. Some ligands will replace coordinated carbon monoxide in the complexes. Phosphine and phosphite ester replacements have been thoroughly studied. Alcohols and amines, hydrogen and cobalt hydrocarbonyl, and oxidizing agents break the cobalt-carbon bond in the alkylcobalt and acylcobalt carbonyls. Insertion reactions occur with a variety of unsaturated organic systems such as olefinic groups, conjugated diene groups, acetylenic groups,

and certain carbonyl groups. Several reactions of alkylcobalt and acylcobalt tetracarbonyls are already known to be useful for the synthesis of organic compounds, and organocobalt carbonyl chemistry will probably find its major applications in this area.

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# Organometallic Reaction Mechanisms

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## I

## INTRODUCTION

During the last decade considerable progress has been made in establishing the mechanistic pathways by which organometallic compounds react. It is the purpose of the review which follows to discuss some aspects of this advance, with emphasis on the unique parallel between coordination chemistry and organometallic chemistry. This parallel is demonstrated in (a) ligand exchange reactions which are equilibrium processes, (b) solvent and salt effects on the path and rate of organometallic reactions, (c) the electrochemistry of organometallics, and (d) in data demonstrating the importance of nucleophilic participation at metal as well as electrophilic attack at carbon in scission and addition reactions of organometallic compounds



Nucleophilic *assistance* at metal is often an important factor in the course of the electrophilic attack at carbon, and indeed several examples exist where nucleophilic attack is necessary for subsequent electrophilic attack or even is rate-determining. It appears that a graded sequence of mechanisms is available and that organometallic compounds make use of a specific pathway depending on the nature of solvent and attacking reagents. In those cases where nucleophile and electrophile are combined in the same molecule, the multicenter pathway is available



This contains two factors which are important to remember—activation of the incipient carbanion by the nucleophilic coordination, and activation of the electrophile by this same step.<sup>3</sup>

<sup>3</sup> The basic concepts may be found in a review by R. E. Dessy and F. E. Paulik, *J. Chem. Educ.* **40**, 185 (1963).

The article is restricted to those organometallic derivatives of the non-transition metals, and to reactions involving scission of a M—H or M—C bond.

## II

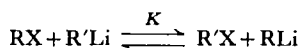
### ORGANOLITHIUM COMPOUNDS

Few detailed mechanistic studies of reactions of organolithium reagents are known, apparently because of the high specific rate constants exhibited by most of these processes, coupled with the sensitivity of these organometallic compounds toward oxygen and water. Nevertheless the last several years have afforded much data which indicate the direction that research in reaction mechanisms in this area, as well as in others, is taking or should take. Specifically, they first involve the problems of structure and the effect of solvent on structure (1-14). This area has been reviewed by Brown (1).

The useful reactions of organolithium reagents that have been studied mechanistically may be conveniently divided into five categories: (a) M—X interchange, (b) M—M interchange, (c) M—H interchange, (d) Wurtz-type coupling, and (e) addition reactions (to olefins, and ketones). Prior to this decade two isolated kinetic reports, on the metallation of anisole, and the addition to ketones, existed (15, 16). Both of these processes seem to require reinvestigation, and possible reinterpretation.

#### A. M—X Interchange

Metal-halogen interchange in the system,



has been studied (17). Recognizing the aggregate nature of organolithium reagents in the solvents employed (ether/pentane and pentane), analysis of the equilibrium constants indicates that the bonding energy associated with a particular RLi in an aggregate is independent of the identities of the other alkyls in the aggregate. The equilibrium constants therefore have been interpreted on the basis of relative carbanion stabilities, the philosophy apparently being adopted that the most electronegative organic groups will tend to reside, at equilibrium, with the most electropositive elements,

permitting maximum possible contribution of the ionic form to the over-all resonance hybrid. This approach has also been used to explain results of the exchange (18, 19)

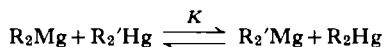


Table I shows the relative  $K$  for the two reactions. Correlation is good except for the vinyl group, and results suggest that an embryonic sequence of carbanion stabilities may be derived from the data. Indeed, Cram (47b) has devised a scale of hydrocarbon acidities from these series.

TABLE I  
RELATIVE EQUILIBRIUM CONSTANTS FOR EXCHANGE REACTIONS

R	$\log K$ $Rmg + \phi hg \rightleftharpoons \phi mg + Rhg$	$\log K$ $RLi + \phi I \rightleftharpoons \phi Li + RI$	$RHgX$ $-E_{1/2}^2$
cyclo-C <sub>5</sub> H <sub>11</sub>	—	6.9	—
iso-Pr	> 6.0	—	3.39
iso-Bu	4.3	4.6	—
<i>n</i> -Pr	—	3.9	—
Et	4.0	3.5	3.37
Me	1.8	—	3.22
$\phi CH_2CH_2$	1.0	—	3.16
cyclo-C <sub>3</sub> H <sub>5</sub>	0.7	1.0	3.13
CH <sub>2</sub> =CH	0.3	-2.4	3.06
C <sub>6</sub> H <sub>5</sub>	0	0	3.04
CH <sub>2</sub> =CH—CH <sub>2</sub>	-0.4	—	—
CCl <sub>3</sub>	—	—	2.87
$\phi CH(CH_3)$	-0.4	—	—
C <sub>6</sub> Cl <sub>5</sub>	—	—	2.48
$\phi CH_2$	-0.7	—	2.20
CH <sub>3</sub> O <sub>2</sub> C	—	—	2.04

In both series the *tert*-C<sub>4</sub>H<sub>9</sub> group is sluggish to exchange. Work in the Rmg/R'hg<sup>4</sup> system indicates that both  $\alpha$  and  $\beta$  substitution markedly decrease the rate at which equilibrium is attained, and together with the

<sup>4</sup> In this review an element symbol in lower case has been used to represent an element at normal valence, but with only a few of the coordinating sites, e.g., hg versus Hg, mg versus Mg.

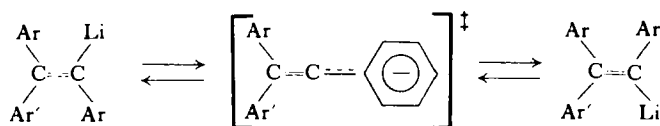


second-order nature of the reaction, suggests a four-center bridge transfer mechanism (19).



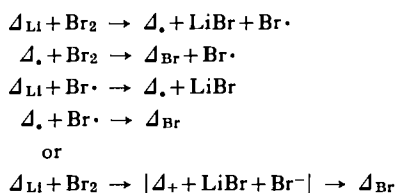
### B. $R^*Li$ Lability

Configurational stabilities of the products of a number of such M-X reactions, as well as from the direct reaction,  $RX + Li$ , have been explored. Alkyl-substituted vinylolithium reagents are configurationally stable (20) under severe conditions (refluxing ether, several hours), but  $\alpha,\beta$ -aryl-substituted reagents are quite labile, possibly suggesting a transition state or intermediate of the following nature:



Recent studies report that solutions of *cis*-stilbenyllithium and *cis*- and *trans*-2-*p*-chlorophenyl-1,2-diphenylvinylolithium in hydrocarbon solvents have very much more configurational stability than in diethyl ether or tetrahydrofuran, the latter producing very rapid isomerization (21). In the former case the position of equilibrium lies largely in favor of the *trans* product, suggesting that steric hindrance is the driving force for the process.

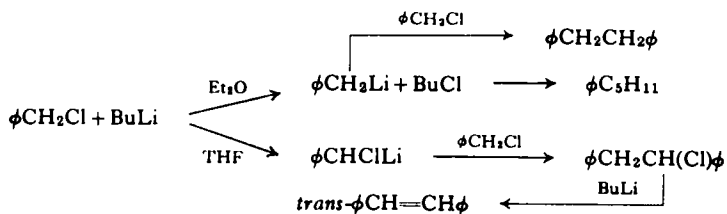
In small ring compounds both Walborsky (22) and Applequist (23) and their co-workers have demonstrated the ability of organolithium reagents to preserve configuration, in media ranging from pure pentane to ether. Surprisingly, the latter study showed that although carbonation proceeds with stereospecificity, brominolysis of the organolithium reagent does not. Two alternate mechanisms have been proposed, one involving a free radical pathway, the other a carbonium ion route.



The authors prefer the free radical mechanism. Some analogy may be found in the brominolysis of organomercurials (24), to be mentioned later.

In the area of aliphatic lithium reagents, Curtin has demonstrated that the butyllithium reagent derived from interchange of (+) or (−) *sec*-butylmercury with 2-octyllithium in pentane is capable of retaining its configuration for long time periods at low temperatures. Carbonation, under conditions of exchange at  $-40^{\circ}\text{C}$  for 4 hours, gave 83% retention. This is reminiscent of earlier work (25) on the stereochemistry of  $\text{RX} + \text{R}'\text{Li}$  interchange. It is unknown whether retention in both steps or two inversions are involved. As with the vinyl reagents, the incorporation of small amounts of ether (6%) led rapidly to complete loss of activity. Unfortunately, no data exist which specifically point to an ionic pathway for racemization.

Besides changing the configurational stability of organolithiums, solvent modification can affect the reaction path. Although benzyl chloride reacts with butyllithium in ether to give the Wurtz coupling products, bibenzyl and amylbenzene, *trans*-stilbene is also a product (26). Isolation of the chlorobibenzyl was possible.



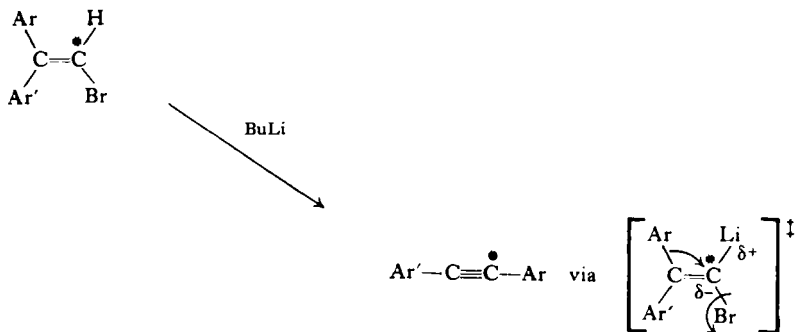
### C. M-H Interchange

The transfer from an M-X to an M-H interchange is to be noted. Curtin *et al.* (27) have also shown that  $\beta$ -bromostyrene undergoes only M-H exchange when treated with butyllithium in ether, but that the principal reaction in petroleum ether is M-X interchange.

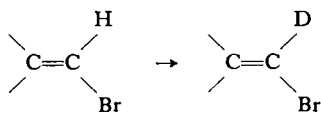
The exact mechanism(s) for M-H interchange are at present unknown (46). In the metallation of benzylic carbon, the excellent stereochemical work of Streitwieser (47a) indicates that the fate of the delocalized carbanion is governed by the philosophies developed by Cram (47b). Since a discussion of work in which carbanion centers, ion-paired with a metal ion, are presumed to be intermediates is beyond the scope of this chapter the reader is referred to the original publications.

### D. Carbanion Rearrangements

Studies on 1,1-diaryl-2-haloethylenes which may undergo M-H or M-X interchange introduce rearrangement reactions.

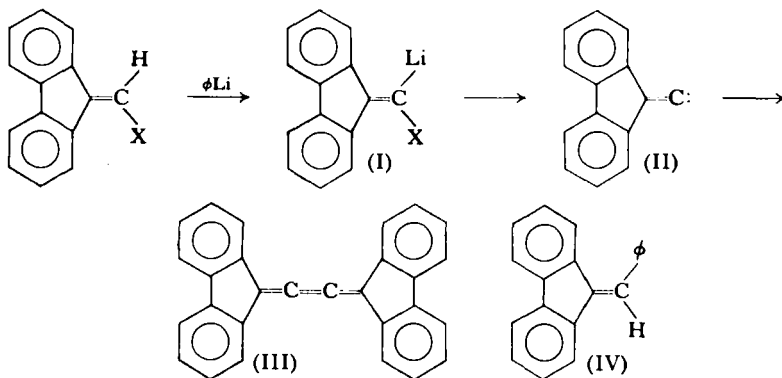


Apparently an intermediate carbene is not involved. Attempts to detect the suspected intermediate  $\text{Ar}_2\text{C}=\text{CLiX}$  failed. The presence of an isotope effect ( $\text{Ph}_2\text{C}=\text{CDBr}$  vs.  $\text{Ph}_2\text{C}=\text{CHBr}$ ) suggests that the rate-determining step is the M-H interchange, followed by a rapid, concerted rearrangement-elimination from a configurationally stable carbanion. The fact that various organolithium reagents, as well as added lithium halides, affect the amount of acetylene formed (presumably by changing the M-X/M-H ratio) is consistent with this interpretation. In *tert*-butoxide/*tert*-BuOD systems the conversion

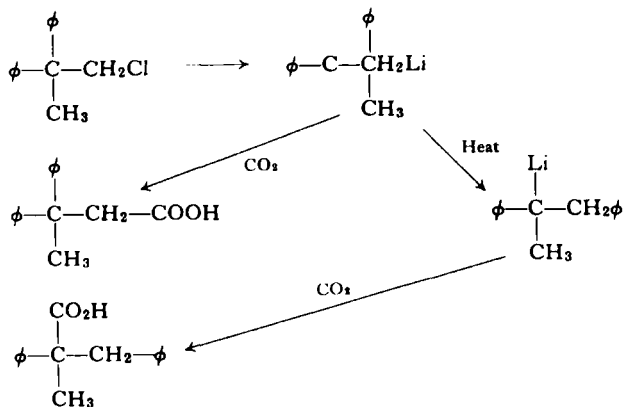


is much faster than rearrangement, suggesting a pre-rate-determining equilibrium involving a vinyl anion which undergoes unimolecular decomposition (28).

Both Curtin and Tonahe and their co-workers (29) have suggested that under other conditions of substrate structure carbenes may be involved. It is presumed that (III) arises from carbene (II) reacting with the halo-lithium intermediate (I), while (IV) is derived from addition of PhLi to the vinyl halide, followed by elimination. A further discussion of organolithium precursors of carbenes appears in Section IV, H.

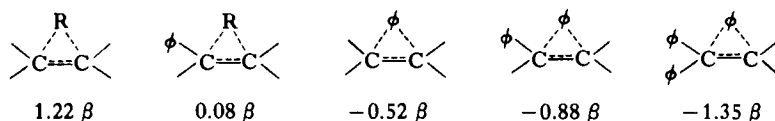


Close analogies to the rearrangement reaction described by Curtin may be found in the more conventional rearrangements of carbanions involving lithium gegenions. After a preliminary study of the 1,2-shift rearrangements induced in 1,1,1-triphenyl-2-chloroethane on treatment with sodium, Zimmerman (35) turned to the following reactions of 2,2-diphenylpropyl-lithium:



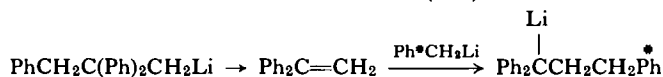
The failure of the magnesium derivative to rearrange, even under forcing conditions, the stability of the lithium reagent at low temperatures, and the facile rearrangement of the potassium compound correlates with the ionic character of the c—m bond, and suggests a carbanionic rearrangement mechanism. To rule out the free radical path, the mixed organolithium reagent,  $\text{Ph}(p\text{-MePh})\text{C}-(\text{CH}_3)\text{LiCH}_2\text{Li}$  was prepared. Phenyl migration predominated, almost exclusively, in agreement with electronic considerations for carbanions and in contradiction with radical migratory aptitudes. Having established a carbanionic rearrangement, Zimmerman calculated,

by LCAO methods, the energetics of such migrations for alkyl and aryl groups. The ordering suggests that the bridging process involved in transfer would be favoured in the sequence

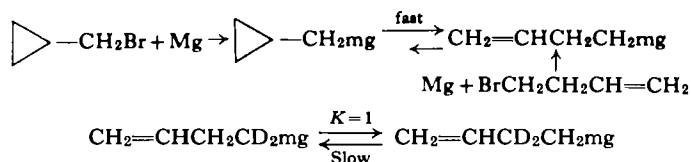


shown with the energy cost (or gain) in units of  $\beta$  given below each transition state, alkyl transfer being highly unfavorable energetically. This suggests that the extensive chemistries built-up around carbonium ion rearrangements and radical rearrangements could be carried over into carbanion analogs. Neighboring group participation in carbanion formation has been suggested (35b).

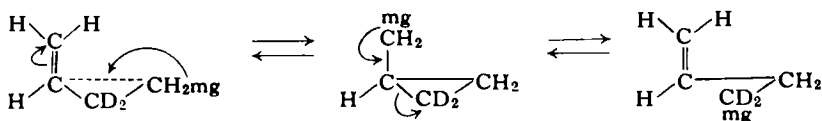
An alternate "rearrangement" mechanism involving intermolecular elimination-addition has been demonstrated (35c).



Little systematic work has been done on this topic, but reports (36–38) on ring-opening processes, akin to the ring expansion processes of the Wagner-Meerwein type, suggest a fruitful area for mechanistic study. Roberts and Mazur (36a) found that the products derived from the Grignard reagent of cyclopropylcarbinyl bromide had predominantly the allylcarbinyl structure, and NMR data showed also that the reagent prepared from allylcarbinyl bromide or the cyclopropylcarbinyl chloride had the same species present. Deuterium labeling indicated that the following equilibrium was involved:



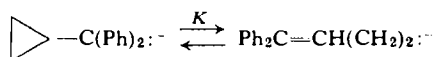
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Lansbury *et al.* (37) have prepared cyclopropylcarbinyllithium by M-X interchange at low temperatures from cyclopropylcarbinyl iodide in

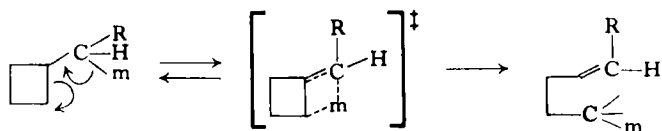
petroleum ether containing 10% ether. Rearrangement to allylcarbinyl-lithium occurs as time, temperature, or ether concentration is increased. The observation that 1,1-dideuterocyclopropylcarbinyllithium does not give rise to species on hydrolysis which contain D in the ring, supports the concept that unlike cyclopropylcarbinylcarbonium ions, cyclopropylcarbinyl carbanions have no nonclassical character.

Data from the system



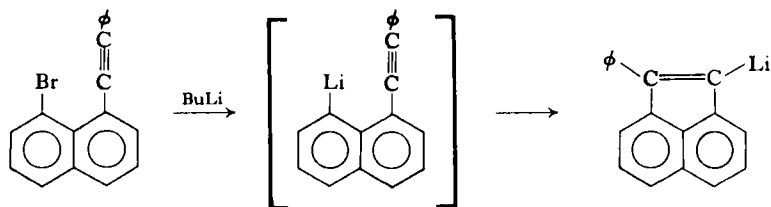
indicate the counterion can affect the value of  $K$ ; for potassium the cyclic form is preferred, while with magnesium or lithium, the olefinic form is favored.

Hill and Richey (38c) have observed similar ring openings in the cyclobutylcarbinyl system, where M is Na, Li, or Mg. They conclude that ring strain is the driving force for reaction. Kinetic studies show that decomposition of the Grignard is first order. The process is insensitive to changes in solvent environment, suggesting that an ionic mechanism is not involved. Absence of hydrocarbon coupling products and the fact that  $\alpha$ -substitution does not affect the rate seem to disfavor a free radical route. Suggested is



This seems supported by the observation that the  $\alpha$ -cyclobutylethyl-magnesium chloride rearrangement gives about equal amounts of *cis*- and *trans*-2-hexene. An incipient olefin  $\pi$ -complex would explain the large apparent amount of *cis* product, considering the thermodynamic stability of the *cis* olefin in comparison with the *trans* product. Of course a transition state in which olefinic character was not highly developed would also explain the observations. The reverse, cyclization process, has also been studied.

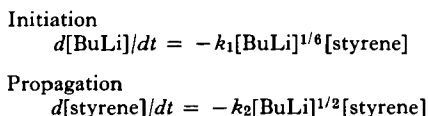
Dessy and Khandil have noted that



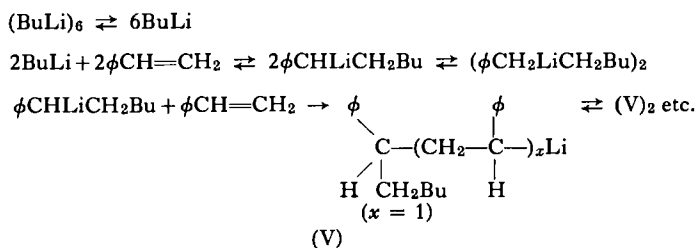
thus opening up a general route to acenaphthylenes. Alkylidenefluorenes may be generated in a similar manner (38d).

### E. Polymerization

The reactions above have involved, often as the implied reverse reaction, the addition of organolithium or organomagnesium across an olefinic linkage. From the principle of microscopic reversibility, the mechanism of ring opening, a four-center process, should have some bearing on such a process. Grignards do not ordinarily add across unsaturated linkages, but organolithium reagents do (39–41). Several studies which shed some light on this problem have been carried out as a result of the interest in polymer initiators, and return us once again to the problem of structure and solvent. One detailed study (39a, b) indicates the following: The polymerization of styrene by butyllithium initiator in benzene involves an initiation and a propagation step

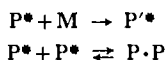


from



However, the kinetics of polymerization of butadiene, isoprene, and styrene with alkyllithium initiators has been studied extensively by Hsieh (39c), and the polymerization rates broken down into initiation and propagation steps. The effects of BuLi concentration, the structure of the butyl group, and the solvent type were studied. The rates of initiation ( $R_i$ ) for the olefins mentioned were determined. For dienes, the order was *sec*-Bu > *iso*-Pr > *iso*-Bu > *n*-Bu > *tert*-Bu. With *n*-BuLi the order was styrene > butadiene >

isoprene. For any particular monomer-initiator combination the order was toluene > *n*-hexane > cyclohexane. The results obtained prove that  $R_i = k_i [\text{RLi}][\text{M}]$  for all three monomers. *The first order relationship between initiation rate and [RLi] does not agree with the data of Worsford and Bywater reported above.* The origin of the discrepancy is not apparent. Other laboratories have begun to doubt the validity of a mechanism involving  $[\text{RLi}]^{1/6}$ . Incidentally the first-order kinetics do not necessarily indicate that the initiators are not associated, they might indicate that activity is independent of association. Initial propagation rates ( $R_p$ ) for the same monomers were obtained with *sec*-BuLi as an initiator. Here initiation is so rapid that propagation alone may be studied. In the case of diene monomers at  $[\text{RLi}] \geq 10^{-2}M$ , and for styrene,  $R_p = k_p [\text{RLi}]^4 [\text{M}]$ . The data are consistent with a mechanism



where  $\text{P}^*$  and  $\text{P}'^*$  are unassociated active polymer-Li and M is monomer, and  $\text{P} \cdot \text{P}$  associated polymer.

These observations, added to the fact that addition of polar solvents to polymerization reactions of butadiene initiated by organolithium reagents in hydrocarbon solvents can change the stereochemistry from one of predominantly *cis*-1,4 to that of 1,2 and *trans*-1,4, suggests that the lithium may form a  $\pi$  complex with the olefin, and if this is sufficiently strong, orient the monomer prior to the incorporation step.

Excellent studies on contact ion pairing in such processes is being provided by Hogen-Esch (39e).

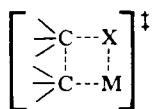
### F. Wurtz Coupling

Returning to the interchange processes listed earlier, one can readily conclude that little is known about the details of any of these processes. The availability of optically active lithium reagents, the modern interpretation of structure, and the effect of solvents seem to urge a reinvestigation of many of these processes only cursorily studied in the past. The Wurtz reactions or M-H interchange are a case in point; Cristol *et al.* (42) have reported that the reactions of PhLi or MeLi with *n*-BuCl and *tert*-BuCl are second order, first in each reagent (the product in each case is different). In the reaction

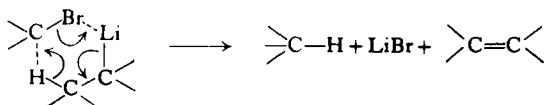
$\text{BuLi} + (+)\text{-2-bromobutane} \rightarrow 3\text{-methylheptane (inversion)} + 98\% \text{ racemization}$   
the observed inversion, albeit a small segment of the final product, is in



disagreement with a mechanism proposed originally for alkylsodiums, which was four-center in nature, thus requiring retention of configuration (43)



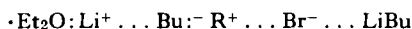
Direct S<sub>N</sub>2 displacement seems indicated for the inversion pathway. However, the large amount of racemization might suggest a radical pathway involving electron transfer processes. Work on the Wurtz reaction accomplished by alkylsodium reagents, also indicates that inversion of configuration (or racemization) is the rule for this process (44). Solvent can, as mentioned previously, direct markedly both the course and rate of organolithium, alkyl halide reactions (45a). In hydrocarbons, butyllithium and 1-bromooctane give predominantly reduction products.



In ether/hexane the coupling reaction takes place, and fits the equation

$$\text{rate} = k_a[\text{BuLi}]_a[\text{RBr}]_a$$

where subscript a's refer to apparent concentrations. Plots of  $\log k_a$  vs.  $[\text{Et}_2\text{O}]$  do not extrapolate back to the origin, but have a positive Y intercept, indicating that very small amounts of ether effect a highly specific solvation phenomenon, in addition to slight changes of  $k_a$  induced by macroscopic solvent properties. The polymeric nature of BuLi in hexane/ether has led to the suggestion of the following interaction (45a):



Brown favors a more subtle interpretation based on coordination of ether to the *hexamer*, a process which should increase the lability of an adjacent alkyl group.

Becker (45b) has observed, in nitrile reactions with Grignards, that basic solvents impede the reaction, apparently by coordinating strongly with the Mg site, blocking entry by the ketone to the coordination sphere, an act necessary for consumption. The effect on the rate of the addition of ethyl Grignard to benzonitrile is remarkable, relative rates for common solvents being THF, 250; Et<sub>2</sub>O, 17.8; THF, 3.65; diglyme, 0.483. There is little doubt that the alkyl group here is also activated (cf. NMR of alkylaluminum

etherates). The solution to the dichotomy is undoubtedly to be found in the polymeric nature of organolithium, where although one site is blocked by the solvent ether, other sites are available for halide coordination. The normal activation by nucleophilic coordination by substrate is augmented by the solvating ether. One area that deserves further attention is the observation that nitrile/Grignard reactions are accelerated by  $\text{LiClO}_4$  or  $\text{Bu}_4\text{NClO}_4$ , apparently due to ion quadrupole interactions (183).

### III

## ORGANOMAGNESIUM COMPOUNDS

### A. Nature of the $\text{—}\overset{\text{>}}{\text{C}}\text{—Mg}$ Linkage

Considerable effort has been exerted in the last decade on the problem of Schlenk-type equilibria and mechanisms in the Grignard area. The background to the area has been well reviewed (48).

The nature of the  $\text{C—Mg}$  bond is much in doubt. On the basis of the similarity of the NMR spectra of phenyllithium, phenyl Grignard, and pyridine, it has been suggested that one is dealing with highly associated ion pairs— $\text{R:}^-\text{Mg}^+$  (49). Indeed the ultraviolet spectra of phenyl Grignard has been interpreted as involving an  $n\text{—}\pi^*$  transition similar to that of pyridine. However, considerable disagreement exists over this interpretation.

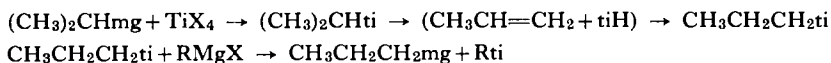
Data derived from experiments involving the configurational stability of Grignard reagents are clear, but their interpretation is not. Vinylic and cyclopropyl derivatives can retain their configuration even in basic solvents, and Walborsky *et al.* (50) have shown that extensive racemization occurs in forming cyclopropyl Grignard reagents via classical routes ( $\text{RX} + \text{Mg}$ ), while preparation from  $\text{RLi} + \text{MgX}_2$  leads to complete retention. A radical-like process for Grignard formation has been proposed. Attempts to prepare optically active Grignard reagents involving  $sp^3$  carbon in symmetric environments have failed ( $\text{RX} + \text{Mg}\rightarrow$ ), although a preliminary announcement has suggested that the exchange route ( $\text{Rmg} + \text{Rhg}\rightarrow$ ) can yield optically active product (51).

Others (52, 53, 54) have used NMR as a tool to investigate this type of phenomenon. In  $(\text{CH}_3)_3\text{CCH}_2\text{CH}_2\text{Mg}$  the protons in question show an NMR signal which changes from an  $\text{A}_2\text{X}_2$ -type spectrum at  $33^\circ\text{C}$  to an

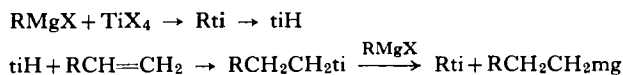
AA'XX' pattern at  $-50^{\circ}\text{C}$ . The observation of two distinct vicinal coupling constants at low temperatures indicates that inversion of configuration at the  $-\text{CH}_2\text{mg}$  center is slow on an NMR time scale. The authors believe that changes in conformational population are not responsible for the thermal change in spectra, and attribute it to inversion at the methylene center. Similar effects are noted in the NMR spectrum of the  $\text{CH}_2$  group of  $\text{Ph}(\text{iso-Pr})\text{CHCH}_2\text{mg}$ , while  $\text{Ph}(\text{CH}_3)\text{CHCH}_2\text{mg}$  shows only magnetically equivalent methylene protons even at  $-75^{\circ}\text{C}$ . These findings have been partially explored mechanistically and although the popular feeling seems to be that the first two results involve rapid inversion due to intermediate carbanion formation, this is not the only possibility, since direct and rapid substitution processes could lead to such findings. Indeed, the work of Roberts (52) and unpublished results (53) of Fraenkel indicate that in the methylbutyl Grignard system the inversion process involves an intermolecular electrophilic displacement of magnesium on carbon by another magnesium species. The process is roughly second order in  $\text{R}-\text{mg}$ .

### B. Transition-Metal-Induced Processes

Deep-seated rearrangements in Grignard systems are catalyzed strongly by small amounts of transition metal impurities (55).



This rearrangement from isopropyl to *n*-propyl Grignard implies that any Grignard may be used to provide the intermediate subvalent titanium compound, and that addition of externally generated olefin would lead to the synthesis of organomagnesium compounds directly from olefins, without the intermediate formation of alkyl halide.

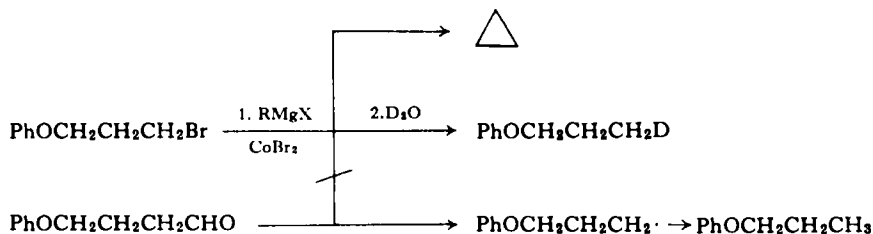


This is indeed realized, often in yields approaching 50%. The Grignard reagent produced is normally terminal, showing that the suggested addition of tiH to the olefin is similar to hydroboration. Internal olefins are inert, thus allowing selective Grignard production.



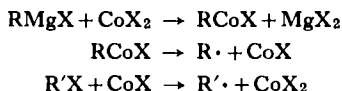
In the aromatic series, surprisingly, styrene yields  $\text{PhCHMgCH}_3$ . Many other catalysts allow this process to occur, often 25 or more cycles per metal atom being observed. It is possible that more active catalyst systems occur, and are the cause of many anomalies found in Grignard chemistry.

Slaugh (56) has shown that in the Kharasch reaction of 3-phenoxypropyl bromide the radical  $\text{PhOCH}_2\text{CH}_2\text{CH}_2\cdot$  does not seem to be the intermediate, but that  $\text{PhOCH}_2\text{CH}_2\text{CH}_2\text{mg}$  would explain the observations.



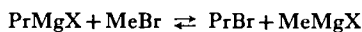
Since it has been reported (57) that transition metal halides will catalyze the  $\text{RMgX}/\text{RX}$  exchange, many of the so-called Kharasch reactions may actually involve transient organomagnesium reagents derived from such processes, and Slaugh has cited the production of bicyclo[3.1.0]hexane from 1,3-dibromocyclohexane and cyclohexene from 1,2-dibromocyclohexane.

It is generally felt that other Kharasch reactions involve radical intermediates, since 2,3-dimethyl-2,3-diphenylbutane is formed when cumene is present, and rearrangement products are observed in the neophyl chloride system, although some of the latter might arise from the carbanion rearrangement reactions described in Section II, D.



The biggest controversy has arisen over whether atomic (colloidal) cobalt is involved, or  $\text{CoCl}$ , and whether the radicals are truly free (58). A partial answer is given by the report (59) that Grignard/ $\text{CuBr}$  mixtures give blood red solutions of long-term stability which exhibit IR and NMR evidence of a highly coordinated (ether and  $\text{RMgX}$ ) organocopper species. Similar findings for  $\text{Ni(II)}$ ,  $\text{Co(II)}$  and  $\text{Fe(III)}$  are given. In reactions of the catalyst systems with alkyl halides, disproportionation and coupling products are found. With ethyl Grignard and ethyl bromide, butane, ethane, and ethylene are produced, but the ratio of disproportionation to coupling is not what

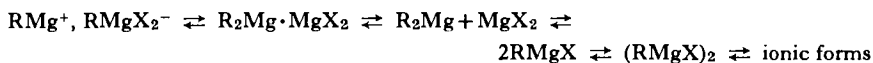
might be expected from either free or caged ethyl radicals. Only about 30% of the reaction appears to involve radical species, the other pathway involving the production of equal amounts of olefin and alkane. This path could be direct  $E_2$  elimination induced by the action of alkide ion on olefin, or to  $\beta$ -hydride ion transfer and reduction (cf. organolithium reduction) of the alkyl halide. In one case the resulting olefin comes from the alkyl halide, in the other it is derived from the organometallic reagent. Simple observation of the source proved difficult since even simple Grignards such as propylmagnesium halide exchanged with methyl bromide in the presence of catalyst.



However  $C^{14}$  labeling showed that in the isopropyl Grignard/isopropyl halide system, the majority, if not all, of the olefin is derived from the organometallic reagent, and only 23% of the propane evolved has a free radical source.

### C. The Schlenk Equilibrium

The final area that can be discussed involves the kinetics and mechanism of reactions of Grignard reagents with ketones, nitriles, Schiff bases, and weak acids. This area is intimately tied to the problem of the structure of the organomagnesium reagent itself and this in turn centers around the values of the equilibrium constants for the processes



particularly in *diethyl ether* solutions.

The fact that the apparent kinetics and rate of reaction of solutions of "EtMgBr" and  $(\text{Et}_2\text{Mg} + \text{MgBr}_2)$  with hexyne, benzophenone, or  $\text{Et}_2\text{CO}$  and iso- $\text{Pr}_2\text{CO}$  are identical has led to the statement that both solutions contain the same specie(s) (60, 61, 71). The conductivity of these two solutions, originally reported to be different (62), has been examined by Vreugdenhil and this physical measurement is about the same for the two alternate methods of preparation (63). Added to the report that dielectric titration of  $\text{MgBr}_2$  with  $\text{Et}_2\text{Mg}$  gives a sharp break at a 1:1 ratio with a dielectric constant equal to that of "EtMg Br" the evidence strongly points to  $\text{Et}_2\text{Mg} + \text{MgBr}_2$  being able to yield the same species as  $\text{EtBr} + \text{Mg}$ . Tracer experiments, using  $\text{Mg}^{28}\text{Br}_2$  and  $\text{Et}_2\text{Mg}$  have indicated that under

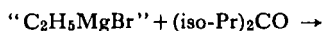
certain conditions no exchange of Mg occurs between the two species, and this fact has been interpreted by many to indicate that  $\text{RMgX}$  does not exist in this system in ether. However, random exchange (64) is often found under conditions that are apparently identical to the no-exchange results, and two possibilities seem to exist: (a) that impurities can result in random exchange (see Section B) and the Grignard structure in this system is best represented by  $\text{R}_2\text{Mg} + \text{MgX}_2$ , or (b) that interaction of  $\text{Et}_2\text{Mg}$  and  $\text{MgBr}_2$  to give " $\text{EtMgBr}$ " structures is normally a slow process unless catalyzed. Unpublished X-ray data (63b) by Vreugdenhil indicate crystals obtained from carefully handled  $\text{R}_2\text{Mg} + \text{MgX}_2$  systems differ from those obtained from  $\text{RX} + \text{Mg} \rightarrow$  systems.

Molecular weight data of many Grignard systems *in ether* have been reported in the last few years (65). In the 1–10 mM range  $\text{Et}_2\text{Mg}$  and the " $\text{EtMgBr}$ " reagent have  $i = 1$ , while  $\text{MgBr}_2$  has an association factor of 1.1–1.15, a value which is independent of added Grignard or  $\text{Et}_2\text{Mg}$ . If these association factors are significantly different so as to be meaningful, then a slow reaction to give " $\text{EtMgBr}$ " structures is a possibility. As the concentration is increased into the molar region very rapid associations occur, leading to  $i = 2$  near 0.5 M. With other Grignards the  $i$  factor increases somewhat more rapidly as concentration is increased, and in a few chloride cases is 2 even at 0.2 M concentrations. If the solubility of  $\text{MgBr}_2$  in ether (about 0.14 M) is taken to be its solubility in  $\text{Et}_2\text{Mg}$  solutions, and the possibility of supersaturation or ionization is ignored, then species such as  $\text{EtMgBr}$  must be invoked, but these factors have not been adequately tested. Recent "trapping" experiments by Ashby (65d) using triethylamine support the existence of an  $\text{RMgX}$  species in ether solutions. It may be possible to arrive at values for the equilibrium constants mentioned above via this route.

NMR measurements have proved of no value (66), and application of IR techniques (67) to ethereal solutions has been largely unfruitful. In THF, however, some success has been met. IR spectra (500  $\text{cm}^{-1}$  region) are identical for  $\text{R}_2\text{Mg} + \text{MgX}_2$  and " $\text{RMgX}$ " and prove to be halogen- and concentration-independent. The band near 500  $\text{cm}^{-1}$  has been attributed to the c-mg stretching frequency. The shape of the band alters as the apparent  $\text{R}_2\text{Mg}/\text{MgX}_2$  ratio ( $\text{R} = \text{Me}$ ;  $\text{X} = \text{Br}, \text{Cl}$ ) is changed, and the data seem best interpreted on the basis of  $\text{R}_2\text{Mg} + \text{MgX}_2 \rightleftharpoons 2\text{RMgX}$ . Calculations indicate that  $K = 4$  (statistical) and that the solubility of  $\text{MgX}_2$  is *higher* than would be expected for pure THF solvent. Similar findings for



was blocked completely, and now the ratio reduction/enolization was invariant to halogen, suggesting that their source is related, as would be expected from the above transition states. However this requires the presence of  $\text{mg}-\text{X}$  in the transition state, even if dimer structure is modified. Employment of a dimer structure indicates that utilization of all the R groups will not be the same. The following results show the product distribution for consumption of the first 50% and last 50% of the R groups in the system described:



	Addition	Reduction	Enolization
First stage	82%	17%	1%
Second stage	18%	51%	31%

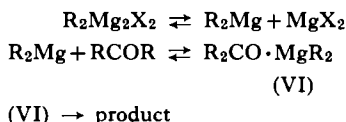
Surprisingly, in the stereoselective reduction of methyl *tert*-butyl ketone by the Grignard derived from (+)-2-methyl-1-chlorobutane or the corresponding  $\text{R}_2\text{Mg}$  compound *no* difference in the stereoselectivity of the first and second stages can be found (69). Rapid equilibria of the type  $\text{RMgOR} \rightleftharpoons \text{R}_2\text{Mg} + (\text{RO})_2\text{Mg}$  have been suggested.

Such a situation has been described by Eliel in the asymmetric reduction of ketones by  $\text{LiAlH}_4$ , rapid disproportionation of the type  $\text{LiAlH}_3\text{OR} \rightarrow \text{LiAlH}_4 + \text{LiAl(OR)}_3$  being involved (70).

Rates and products of the reaction of diethyl and diisopropyl ketone with  $\text{Et}_2\text{Mg}$ , "EtMgBr," and "EtMgOR" have been studied (71). The so-called second stage of reaction of ketones with  $\text{Et}_2\text{Mg}$  gave predominantly enolization and reduction, in comparison to the first stage (comparison of  $\text{Et}_2\text{Mg}$  and EtMgOR). This agrees with earlier observations that  $\text{MgBr}_2$  increases yields of addition products in Grignard reactions. However, kinetic observations clearly show that  $\text{MgBr}_2$  inhibits the reaction of  $\text{Et}_2\text{Mg}$  with ketones. The "EtMgOR" intermediates also proved to be less reactive than  $\text{Et}_2\text{Mg}$ . The report (70) that the kinetics seem to fit the expression,  $\text{rate} = k[\text{Et}_2\text{Mg}_2\text{Br}_2][\text{ketone}]$  better than  $\text{rate} = k[\text{EtMgBr}][\text{ketone}]$  is, of course, mathematically impossible. In any case it is suggested that the  $\text{MgBr}_2$  functions either to tie up RMgOR, preventing it from serving as a base for enolization processes, or that it catalyzes symmetrization of RMgOR. It



does not appear in the transition state for addition, etc. (see above). Because one literature report (without experimental data) claims that acetone reacts with methyl Grignard via a path first order in Grignard alone (72), the following mechanistic scheme was proposed:

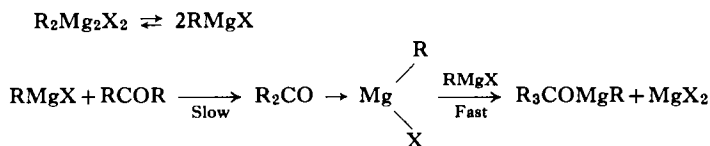


The kinetic order would depend on whether dissociation of the dimer species, complexation, or R transfer was rate-determining.

Smith (73) has detected two ketone-Grignard complexes—the reacting solution of 2,4-dimethylphenyl-*p*-methoxyphenyl ketone and methylmagnesium bromide shows a new UV absorption ( $\lambda_{\text{max}}$  315 m $\mu$ ) with the ketone band, and the new complex band, disappearing rapidly, and at the same rate, following first-order kinetics. Substitution of isopropyl groups for methyl leads to a stable complex, from which data for formation constants can be obtained ( $\text{MgBr}_2$ ,  $K = 6.5$ ;  $\text{MeMgBr}$ ,  $K = 3.7$ ;  $\text{Me}_2\text{Mg}$ ,  $K = 1.3$ ). It is claimed that the spectrum of the complex “ $\text{MeMgBr}$ ”·ketone cannot be derived by summation of the spectra for  $\text{Me}_2\text{Mg}$ ·ketone and  $\text{MgBr}_2$ ·ketone.

In a system involving thioketone, data similar to the above have been found.

Ashby (74) has attempted to reinterpret the available literature data, and has expressed strong support for the process



Such a mechanistic scheme has the merit that it adequately provides an explanation for the fact that benzophenone, even in THF, can utilize only 50% of the available R groups (75). However an intermediate from reaction of dimer, either unsymmetrical ( $\text{R}_2\text{Mg} \cdot \text{MgX}_2$ ) or symmetrical  $(\text{RMgX})_2$ , can accomplish the same result. Anteunis has suggested that in the reaction of  $\text{Me}_2\text{Mg}$  with benzophenone, where also only 50% of the available alkyl groups are consumed, the product of a rapid di-addition  $\text{Ph}_2(\text{Me})\text{COMgOC}(\text{Me})\text{Ph}_2$  could complex with a mole of  $\text{Me}_2\text{Mg}$  and

interfere with its subsequent use. Such coordination of RMgX with the product of direct addition of RMgX to a ketone,  $R_3COMgX$ , would also explain this type of result. Ashby has explained the slower rate of addition of RMgX to ketones, compared with  $R_2Mg$ , on the basis of solvent/substrate competition for the sites on the reagent. The RMgX is a stronger Lewis acid than  $R_2Mg$  and will therefore form tighter coordination bonds with solvent, excluding the substrate. Smith's data would seem to refute this (73), RMgX having a higher formation constant with substrate than  $R_2Mg$ .

Thus four mechanistic pathways have been described, all in basic disagreement with each other. It is very possible that the often expressed warning (76) that the structure of the Grignard reagent may depend on solvent, R, and X may well carry over into its mechanistics with  $R_2'CO$ , and that in fact no unique mechanism exists. Other ketone kinetic data are available, but do not seem pertinent at this point, because of their limited or tentative nature, or because they do not reveal information that could be of value in distinguishing mechanistic pathways.

The kinetics of the reaction between methylmagnesium bromide and benzophenone in ether/benzene has been explored (77) and a rate process consistent within runs with the kinetic expression,  $\text{rate} = k[RMgX]^2[\text{ketone}]$  reported. Unfortunately over the short concentration spans employed "between runs" the  $k$ 's are inversely proportional to Grignard concentration. In THF the same reaction is second order within a run, if only initial points are considered, the second half of the R groups being utilized very slowly (61). In the ether/benzene system  $Me_2Mg$  reacts with benzophenone by a process claimed to be third order, but the intended mechanism is not clear, nor do the data support the third-order expression. Initial rates in THF are claimed to be second order (61).

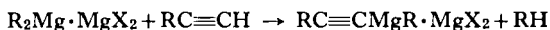
### *E. Addition to Nitriles and the Azomethine Link*

Storfer and Becker (78) have studied the addition of "EtMgBr" and  $Et_2Mg$  to benzonitrile in THF and reported that only one-half of the available alkyl groups are utilized under stoichiometric conditions via a second-order pathway. Similarly second-order kinetics are reported for the reaction of benzonitrile with *n*-butyl Grignard in ether (79), and the reaction of pivaloylnitrile and ethyl Grignard (for over 60% utilization of R groups) (80). Apparently the fact that RMgX reacts faster than  $R_2Mg$  with nitriles has been forgotten in re-evaluating literature data.

Schiff bases also add Grignard reagents via a process utilizing only 50% of the available R groups easily (81), the process involving second-order kinetics and a four-center transition state. The reaction of Grignard reagents with weak acids, such as acetonitrile and alkynes has also been studied (84, 82).

### F. Miscellaneous Reactions

Alkyl Grignards appear to react with hexyne in ether by a second-order process. This has been interpreted to mean that the  $k_1/k_2$  ratio in the following scheme is 2, at which point the consecutive competitive process involved will appear to be simple second order in RMgX and alkyne (82).



(VII)



However, if RMgX species are involved the order is straightforward. From dielectric constant measurements, aryl Grignards appear to react by a second-order process in ether, first order in each reactant, with  $\rho = -2.5$ . However, measurements involving gas chromatography techniques indicate a process that is first order (82), although the critical reagent was not determined by varying initial concentrations. The addition of THF is reported to yield a second-order process that is *slower* than the first-order route. Surprisingly, basic solvents accelerate the reaction of diethylzinc with terminal acetylenes (83).

Finally the kinetics and activation parameters for the reaction  $Me_3SiX + RMgX \rightarrow Me_3SiR$  have been determined, and are consistent with a second-order, four-center transition state (84).

## IV

### ORGANOMERCURY COMPOUNDS

#### A. Subvalent Organomercurials

Gowenlock (90), following Kraus' (91) initial work, showed that a large number of thermally labile materials analyzing as RHg could be obtained at a cathode in RHgX/NH<sub>3</sub> systems. On the basis of a lack of ESR signals, and since thermolysis yielded  $R_2Hg + Hg$ , Gowenlock proposed a three-dimensional cubic lattice with alternate R and Hg units. On the basis of high electrical conductivity Coates, however, prefers a system of RHg<sup>+</sup> units



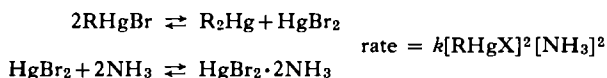
TABLE II

## ACTION OF SYMMETRIZING AGENTS

Symmetrizing agent (s.a.)	Stereochemical outcome (94-99)
$\text{N}_2\text{H}_4$ $e$ $\text{Na}_2\text{SnO}_2 (?)$	} Racemization
$\text{Na}_2\text{S}_2\text{O}_3$ $\text{NH}_3$ $\text{Mg}$	
	} Retention

Coordination of mercurial species is certainly involved in several of these processes. Although the strictly inorganic compounds of mercury form well-defined coordination complexes with amines, phosphines, sulfoxides, phosphine oxides, and amine oxides, particularly when a noncoordinating gegenion for mercury is employed, coordination numbers up to six having been observed (86), the coordination chemistry of organometallic derivatives of mercury is just developing (87-89).

The only kinetic study performed (98), has been soundly criticized (97). Reutov (98) concluded that in the symmetrization of esters of  $\alpha$ -bromomercuriphenylacetic acid by ammonia in chloroform the reaction was best described as



The kinetic form implies a rate-determining second step, but is incorrect for the mechanism written, and Jensen (97) has pointed out that the second step is too rapid to be rate-controlling. Two possible alternate mechanisms are

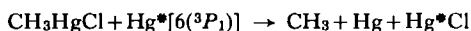


These are completely tentative since preliminary work suggests repression of rate by  $\text{R}_2\text{Hg}$ . Thus growing doubts should also be felt about the other

exchange processes centering around mercury, and the role of metallic mercury,  $\text{RHg}$ , and  $\text{HgX}_2$ ,  $(\text{HgX})_2$  species should be further examined. For example, the pyrolysis of bis(organomercurials) has revealed the dual mechanism (100).



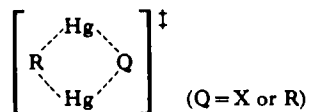
while the  $\text{Hg-6}(^3P_1)$  photosensitized decomposition of methylmercuric chloride vapor has been suggested to involve (101)



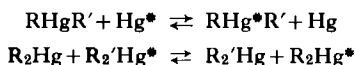
### C. Exchange Processes

Wright (102) has pointed out that the exchange reaction  $\text{R}_2\text{Hg} + \text{R}_2'\text{Hg} \rightleftharpoons 2\text{RHgR}'$  seems to be greatly accelerated by the gray precipitates usually accompanying partially decomposed or oxidized samples, and he concludes that an  $\text{HgX}/\text{Hg}$  aggregate is responsible. Exchange experiments indicate that ligand transfer between the subvalent  $\text{RHg}$  and  $\text{Hg}$  is exceedingly fast (99, 250).

In pioneering studies, Reutov (98a) has reported that both  $\text{R}_2\text{Hg}$  and  $\text{RHgX}$  species undergo a rapid exchange with  $\text{Hg}^{203}$ , and a transition state of the following type has been written:



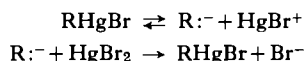
Pollard has supported this view with detailed data (98b). Involvement of  $\text{RHg}$  species, or  $\text{HgX}/\text{Hg}$  in this process cannot be discounted, since the work on symmetrization described above suggests that stereochemistry could be retained, as is observed in these exchange processes. Some support for such a four-center transition state is based on the processes,



no cross products being observed. Mass spectral studies on the exchange  $\text{Me}_2\text{Hg} + (\text{CD}_3)_2\text{Hg} \rightleftharpoons 2\text{CD}_3\text{HgCH}_3$  show the indicated unsymmetrical species (103), suggesting that the original observation in the aromatic series may have been the result of the isolation procedures utilized, these

favoring symmetrical species. As Wright has pointed out, it is extremely difficult to obtain halide-free bis(organomercurials), and halide-free solutions of  $\text{RHgX}$ . It is conceivable that even in exchanges of the type  $\text{R}_2\text{M} + \text{R}_2\text{Hg} \rightleftharpoons$  these factors are important. Both Wells and Kitching (104), and Rausch (105) have noted that in  $\text{RHgI}$  and in some  $\text{RHgBr}$  compounds the usual  $\text{Hg}^{199}\text{--H}^1$  spin-spin coupling pattern is not observed. Moreover Winstein (106) has noted that in allylmercuric iodide, the NMR pattern is altered from that expected of a long-lived  $\text{C--hg}$  linkage to that of the 4:1 pattern of a rapidly flipping allyl configuration by the presence of traces of impurities.

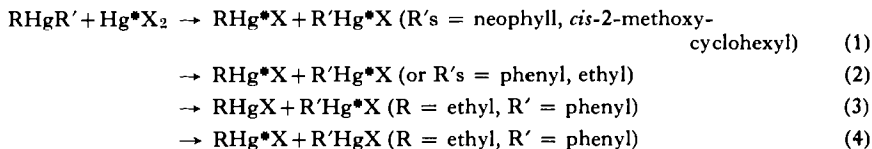
Perhaps such impurities are also the source of many of the anomalous " $\text{S}_{\text{E}}1$  processes"



Nucleophilic catalysis by halide ion would be most reasonable, and such possibilities have been realized in studies (118g) on deoxymercuration, and suggested by the late Professor Hughes for apparent  $\text{S}_{\text{E}}1$  processes involving scission of the  $\text{c--hg}$  bond in some  $\text{--COCH}_2\text{HgX}$  compounds (107).

Ingold has examined loss of activity and acquisition of radiomercury in the exchange of  $\text{Ph}(\text{EtO}_2\text{C})\text{C}^*\text{HHgBr}$  with  $\text{Hg}^*\text{Br}_2$ . The reaction is claimed to be first order in mercury substrate, and zero order in  $\text{HgBr}_2$ . Rate of racemization and incorporation of radioactivity are identical, in agreement with  $\text{R}^*\text{HgBr} \rightleftharpoons \text{R:}^- + \text{HgBr}^+$ ,  $\text{R:}^- + \text{Hg}^*\text{Br}_2 \rightarrow \text{RHg}^*\text{Br} + \text{Br}^-$ . The reaction is *strongly catalyzed by halide ion*, and pre-rate-determining complexes,  $\text{RHgBr}_3^{2-}$  are suggested. The observation that the reaction  $\text{Et}_2\text{TlBr} + \text{sec-Bu}_2^*\text{Hg} \rightleftharpoons \text{Et}_2\text{-sec-BuTl} + \text{sec-Bu}^*\text{HgBr}$  proceeds with racemization, via a first-order process (zero order in  $\text{R}_2\text{TlX}$ ) is also pertinent. An intermediate, rapidly racemizing  $\text{R:}^-$  is assumed (108).

Finally, it is possible that such halide, or subvalent mercury forms are the source of the conflicting data (109–112).



Impurities present in the reaction, but absent in the controls of the first two reactions would have led to the observed data. In the related series, (2)–(4), there is little doubt that (3) is correct (99).

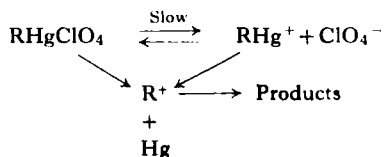
A large number of M-M exchange processes, some involving mercury, have been reported on, and recently reviewed (137). Some of these exchanges are quite slow (days), other are rapid in NMR time. Usually retention of geometrical configuration is noted. Little is known concerning their mechanistic pathways, although some progress in the derivatives of the heavier Group III elements has been made by Oliver.

#### D. $\text{RHg}^+$ Species

Although evidence for  $\text{RHg}^-$  is lacking, and the structure of  $\text{RHg}$  is in doubt, there is clear data concerning  $\text{RHg}^+$ , or rather its ion-paired counterpart,  $\text{RHg}^+, \text{ClO}_4^-$  (113, 114). Jensen observed that many anomalous reports in the literature concerning solvolytic-like decomposition reactions of alkylmercuric halides might be explained by a formulation



Indeed  $\text{RHgOAc}$  compounds, in acetic acid, react slowly by first-order kinetics to give alkyl acetate, mercury, and olefin. Addition of catalytic amounts of perchloric acid gives rise to a fast pseudo-zero-order process ( $k\alpha[\text{HClO}_4]$ ) while large amounts of perchloric acid lead to a very rapid first-order process. The data are best accounted for by the expression



The reaction rate is extremely sensitive to the structure of R, the nature of the solvent, and the available anion. It has been pointed out that reactions of  $\text{RHgX}$  in acid environments may take two courses, depending on these factors,



the first involving in part electrophilic attack on carbon, while the latter is a nucleophilic process of undetermined nature. Jensen has preferred to view the latter as an  $\text{S}_{\text{N}}1$  process in which, because of the bulk, and solvating nature of the mercury, the generated carbonium ion is little solvated, the carbon atom in question developing a high partial positive charge in the transition state. Tables III-V point out the source of this interpretation.



TABLE III  
RELATIVE SOLVOLYSIS RATES OF  $\text{RHg}^+$  SPECIES

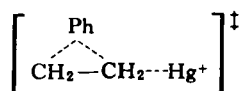
$\text{C}_6\text{H}_{11}\text{HgClO}_4 \xrightarrow[25^\circ\text{C}]{\text{Solvent}}$		$\text{RHgClO}_4 \xrightarrow[25^\circ\text{C}]{\text{HOAc}}$	
Solvent	$k_{\text{rel}}$	R	$k_{\text{rel}}$
HOAc	1	Me	1
EtOH	0.017	Et	$1.2 \times 10^3$
Dioxane	0.6	<i>n</i> -Bu	$1.7 \times 10^3$
Acetone	0.20	iso-Pr	$4.1 \times 10^7$
HOH	0.098	<i>sec</i> -Bu	$8.1 \times 10^7$
		$\text{C}_6\text{H}_{11}$	$1.3 \times 10^8$
		<i>tert</i> -Bu	$6.6 \times 10^{12}$

Neighboring group participation is felt strongly (Table IV).

TABLE IV  
RELATIVE SOLVOLYSIS RATES  
OF  $\text{RHg}^+$  SPECIES

$\text{Ar}-\text{CH}_2\text{CH}_2\text{HgClO}_4 \xrightarrow[75^\circ\text{C}]{\text{HOAc}}$	
Ar	$k_{\text{rel}}$
H	1
Ph	5
<i>m</i> - $\text{CH}_3\text{C}_6\text{H}_4-$	18
<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4-$	59

Presumably structures of the following type are implied:



Finally, some evidence of nonclassical onium ion participation has been presented (Table V).

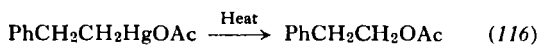
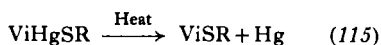
TABLE V  
RELATIVE SOLVOLYSIS RATES OF  
RHg<sup>+</sup> SPECIES

$\text{RHgClO}_4 \xrightarrow[25^\circ\text{C}]{\text{HOAc}} \text{ROAc (+ some olefin)}$	
R	<i>k</i> <sub>rel</sub>
Cyclopentyl	1
<i>trans</i> -4- <i>tert</i> -Butyl cyclohexyl	0.08 (equatorial)
<i>cis</i> -4- <i>tert</i> -Butyl cyclohexyl	1.6
Cyclohexyl	0.82
<i>endo</i> -Norbornyl	0.033–0.029
<i>exo</i> -Norbornyl	55–110
Nortricyclyl	34

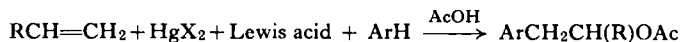
D-(+)-*sec*-Butylmercuric bromide gives mostly racemized, but partially inverted *sec*-butyl acetate under similar conditions, and *n*-butylmercuric perchlorate gives 16% rearranged acetate.

These facts are all consistent with the S<sub>N</sub>1 scheme, but since both allyl and benzyl halides react directly with mercury to give the organomercuric halides, and at the DME these two halides show only the characteristics of the corresponding mercurial, it is interesting to speculate on the reality of ion polarization pairing, similar to ion pairing. All of the philosophies of ion pairing, such as internal return, and intimate/solvent-separated pairing would be applicable. The low ionization potential of Hg, suggesting its large polarizability, adds validity to the concept, and the available data do not preclude the idea.

The general type of mechanism does offer, however, an explanation for the previously reported synthetic findings.



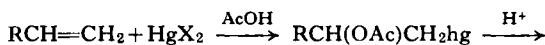
The former are thermal reactions and may involve radical routes. The latter process is the last step in a unique synthetic sequence developed by Ichikawa (116).



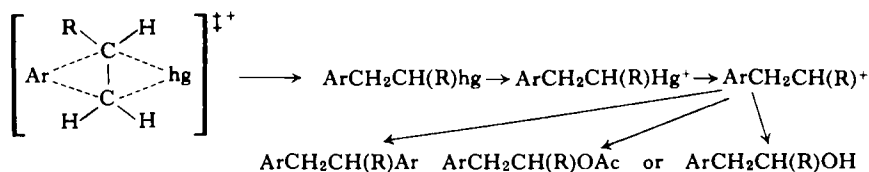
It is known that the intermediate is an organomercurial,  $\text{ArCH}_2\text{CH(R)HgX}$ , and since arylation is at the primary carbon, rather than the secondary one, he has preferred onium ion (IX) to an open carbonium ion (X)



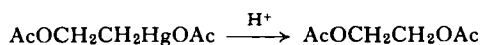
as the arylating agent. Presumably (see Section E) these are derived from the olefin-mercury salt addition products or formed directly.



As onium ions they can serve as excellent reagents for electrophilic substitution on the aromatic ring via the transition state shown,



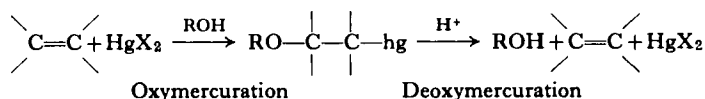
from whence it is an easy, analogous route to the final product. The observation of diarylated product is easily incorporated into the scheme. Ichikawa has argued strongly for an alternate path involving  $\text{RHgHgOAc}$  intermediates, but this, in light of Jensen's work on  $\text{RHg}^+$ , and the strength of neighboring group effects in  $\text{PhCH}_2\text{CH}_2\text{Hg}^+$ , seems unwarranted. He has similarly attempted to interpret the reaction



in a complex manner, but Winstein has observed that certain oxymercurials, such as the 2-methoxycyclohexylmercuric acetates undergo solvolysis to diacetates via carbonium ion intermediates (123).

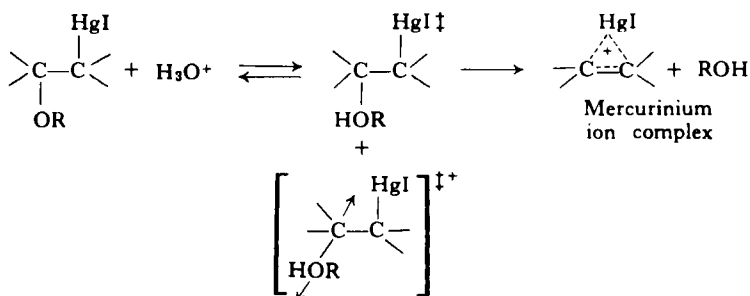
### E. Oxymercuration-Deoxymercuration

The problem of the oxymercuration reaction, and the deoxymercuration process, alluded to above, has only begun to resolve itself in the last few years. The problem has been fundamentally one of assigning stereochemistry and mechanistic pattern to the processes



In 1958, using NMR spectroscopy Cotton and Leto (117) unambiguously established  $\sigma$ -bonded structures for the oxymercuration products, eliminating the  $\pi$  complexes often suggested. Elegant kinetic studies (118), coupled with NMR studies (119), finally gave a firm footing to configurational assignments beginning about 1960.

Kreevoy studied in depth the deoxymercuration of  $\text{CH}_3\text{CH}(\text{OR})\text{CH}_2\text{HgI}$  with perchloric and acetic acids in methanol, and found that the process was pseudo-first order in mercurial, with  $k \propto [\text{HA}]$ . Specific hydronium ion catalysis was involved, and solvent HOH/DOD isotope effects were those predicted by the Butler equations for a pre-rate-determining proton transfer. Further studies on what had been termed  $\alpha$ - and  $\beta$ -2-methoxycyclohexylmercuric iodides under similar conditions, led to similar findings concerning the solvent isotope effects, and correlation of  $\log k$  with  $-H_0$ . This suggested that the transition state differs from substrate only by a proton.



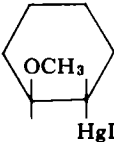
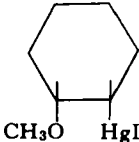
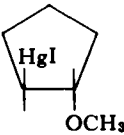
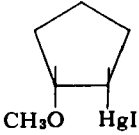
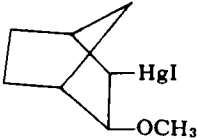
For open-chain and *trans* structures

This was substantiated by later work on secondary deuterium isotope effects in deoxymercuration. Coplanarity of the two carbons, and the RO and HgX functions is implied. However, thermodynamic parameters for

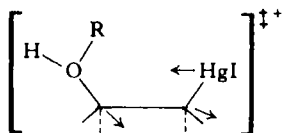
deoxymercuration of the  $\alpha$  and  $\beta$  forms established that although the entropy terms were comparable, the activation enthalpy for the  $\beta$  form was 22 kcal/mole higher than that for the  $\alpha$  form. Kreevoy concluded that this could only be due to the  $\alpha$  form having the *trans* structure, the  $\beta$  form being *cis*. The lack of preference of  $\text{-HgX}$  and  $\text{RO}$ , for axial vs. equatorial positioning would permit *trans* positioning of the groups going into the transition state in the  $\alpha$  form and synchronous  $\text{C-O}$  and  $\text{C-Hg}$  bond scission. On the other hand the *cis* form would of necessity require prior  $\text{C-O}$  scission, to avoid non-

TABLE VI

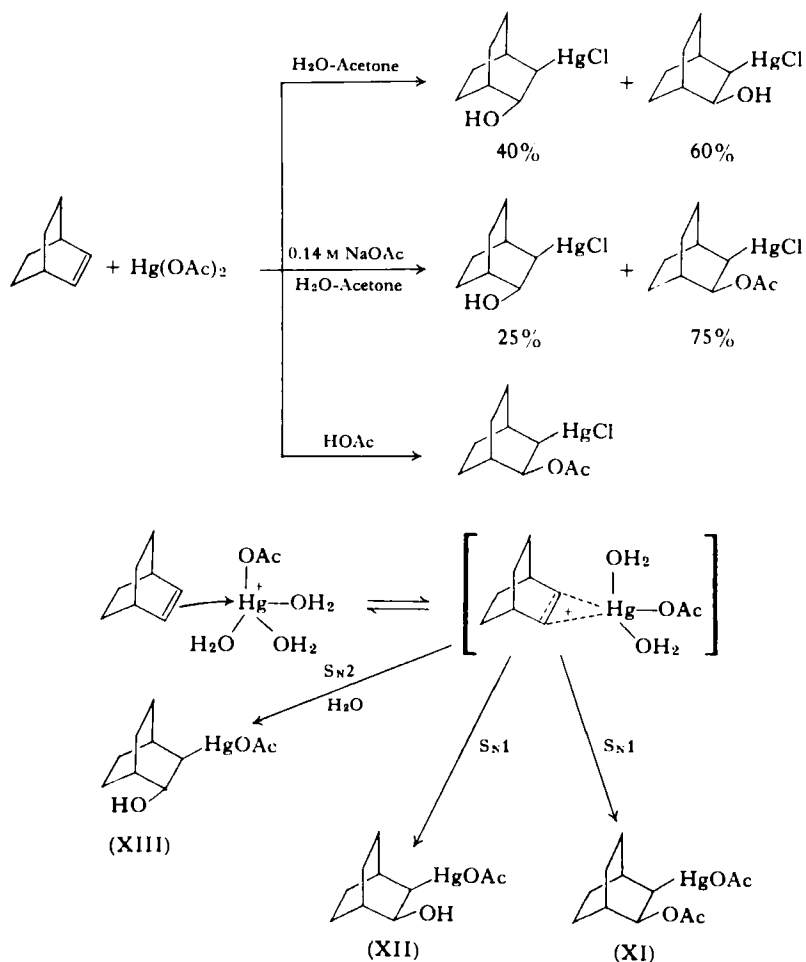
THERMODYNAMIC CONSTANTS FOR DEOXYMERCURATION

Compound	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (cal/mole - degree)
$\text{CH}_3\text{OCH}_2\text{CH}_2\text{HgI}$	19.5	0.1
	17.7	4.6
	26.2	4.5
	15.1	-3
	19.9	-4
	21.0	2.8

bonded interactions between OR and HgX in the only coplanar structure open



These assignments were opposite to those suggested earlier and indicate that oxymercuration in unstrained rings is *trans*, coinciding with conclusions made from NMR observations. The latter work also established that oxymercuration of norbornene was *exo-cis*. Table VI shows that indeed

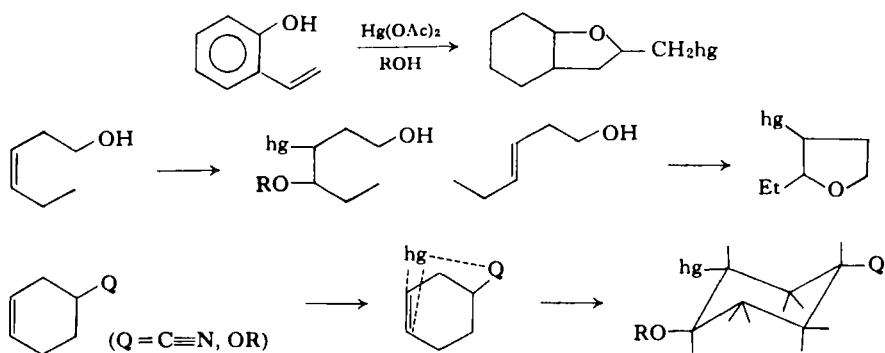


*cis* and *trans* deoxymercuration have unique thermodynamic characteristics.

Using these assignments as guide posts Traylor (120) developed a method of assigning configuration to oxymercuration generally, recognizing that hydroxymercurials whose hydroxyl stretching frequencies differed from the parent alcohol by less than  $10\text{ cm}^{-1}$  were *trans*, while those that differed by more than  $18\text{ cm}^{-1}$  were *cis*. With this as a tool the oxymercuration of bicyclo[2.2.2]octene was studied. Apparently (120) the course of oxymercuration depends on the strain in the olefin employed and in open-chain and strain-free cyclic olefins the addition is preferentially a *trans* one, due to an  $S_N2$ -like attack of solvent nucleophile on a mercurinium ion intermediate (cf. Kreevoy on deoxymercuration). When strain prevents the twist necessary to allow backside attack in sterically crowded cyclic olefins frontside collapse can occur. The results are consistent with *cis*-oxymercuration in aqueous solution producing some acetate product whereas *trans* oxymercuration do not, unless the solvent is a very poor nucleophile. Since no rearrangements of the Wagner-Meerwein type are noted this suggests that no open carbonium ion intervenes in the reaction.

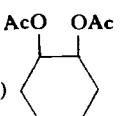
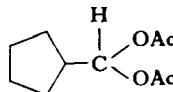
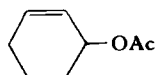
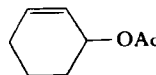
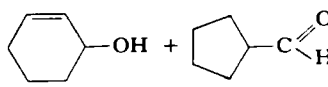
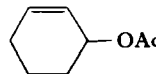
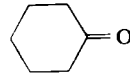
Oxymercuration of norbornadiene leads to the norbornene skeletal product in the kinetically controlled step, but this is readily converted in the presence of traces of  $\text{Cl}^-$  to the nortricyclene skeletal product (126b).

Oxymercuration can be affected by functional groups in close proximity to the olefin in the following manner (121, 122):



In agreement with the above formulations one aspect of oxymercuration that needs further elucidation is its role in oxidation processes. In treatment

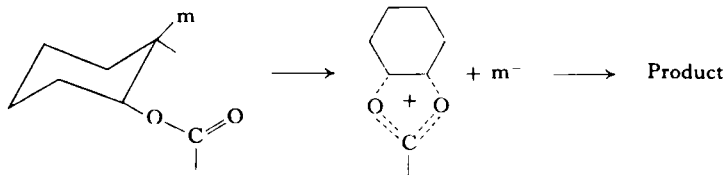
TABLE VII  
CYCLOHEXENE OXIDATION PRODUCTS

Salt	Reaction in	
	Acetic Acid	Aqueous suspension
$\text{Ti}(\text{OAc})_3(\text{TiCl}_3)$	<p><i>cis</i> (1%) and <i>trans</i> (~ 40%)</p>   <p>(50%)</p>  <p>(10%)</p>	Similar pattern
$\text{Hg}(\text{OAc})_2[\text{Hg}(\text{OAc})_2]$		
$\text{Pd}(\text{OAc})_2(\text{PdCl}_2)$		

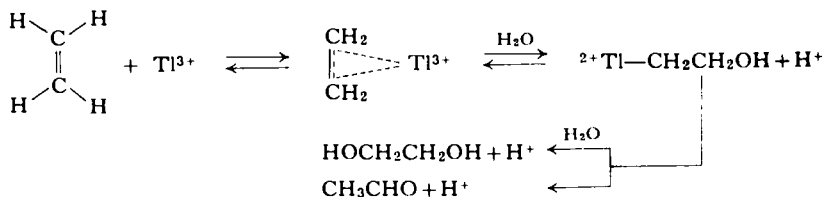


of cyclohexene with mercuric acetate, or thallic or palladous salts in various environments, the products shown in Table VII are observed (123a).

Visualized for the acetic acid environment is a demetallation step with acetoxonium ion participation. The source of allylic product is not certain, but it should be noted that the allylic oxidations reported seem to involve double bond migration (124), as this might imply.



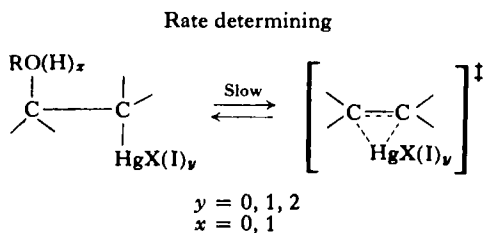
The kinetics of thallic ion oxidation of olefins has been studied (123b). The reaction is first order in ethylene and in thallic ion, and strongly accelerated by added salts, (cf. mercuration of benzene in this section). The lack of proton inhibition and variations in rate as a function of olefin structure, which parallels acid-catalyzed olefin-hydration rates, suggest an activated complex in which the  $\pi$ -complex is moving to a  $\sigma$ -bonded thallium compound with a *high degree of localized carbonium ion character*, in contrast to oxymercuration. The product-determining step may be, in aqueous solution, a concerted loss of Tl(I) and hydride transfer from neighboring carbon (carbonyl products) or attack by water (glycol products).



Similar concepts are being proposed by Ouelette (123c) to explain oxidative cleavages of cyclopropanes by lead or thallium salts. This is an example of the broad scope of the oxymetallation reaction, as well as its counterpart, the deoxymetallation process.

Deoxymercuration, and hence oxymercuration, still presents many pitfalls to broad generalizations. Kreevoy and Turner (118g) have shown that by judicious choice of substrate deoxymercuration can be solvolytic in nature, or involve acid catalysis with conucleophilic catalysis (or assistance)

by one or two iodide ions, or be solvolytic with assistance by one or two iodide ions. Rate-determining formation of the mercurinium ion still seems to be involved. This is an excellent example of combined electrophile/nucleophile attack in the reactions of organometallic compounds



#### F. $\text{C}-\text{Hg}$ Bond Cleavage

This concept is well illustrated in the cleavage of  $\text{C}-\text{Hg}$  bonds by acids and  $\text{HgX}_2$ . In general, the literature seems to support a duality of mechanisms for attack of an electrophile/nucleophile pair on the  $\text{C}-\text{Hg}$  unit. In aprotic environments of low dielectric constant biphilic attack seems involved



while in protic environments where the nucleophile activity is decreased by solvent interaction, attack by the electrophile is rendered more important, some solvent participation being involved (125) (cf. Section VI, C).

The most important criterion that could be examined in these cases involving electrophilic attack at carbon is the stereochemistry. Cleavage of  $\text{Rhg}$  bonds by  $\text{X}_2$ ,  $\text{HX}$ , and  $\text{HgX}_2$ , where  $\text{R}$  is *sec*-butyl, *sec*-octyl, *cis*- or *trans*-2-methoxycycloalkyl, *cis*- or *trans*-4-alkylcyclohexyl, or (1)-menthoxy- $\alpha$ -mercury-bis(phenyl)acetate has been examined. Cleavage by halogen appears to involve two possible mechanistic pathways, one free radical in nature, leading to racemization, the other involving an unspecified ionic pathway showing retention of configuration (126, 127, 96). Cleavage by  $\text{HgX}_2$  (127, 128, 129) has in all cases been reported to give retention of configuration. The stereochemistry of cleavage by acids (127) appears to depend upon the anion of the acid and on the solvent (Tables VIII and IX).

TABLE VIII

ACID CLEAVAGE OF  
 $\text{DI}[(1)\text{-}i\text{-BUTYL}]\text{MERCURY}$ , ( $\alpha$ ) =  $-20.9^\circ$   
 ( $\alpha$ )

Acid	Solvent	Recovered $\text{R}_2\text{Hg}$ ( $\alpha$ )	% Retention RD
DOAc	DOAc	$-5.26^\circ$	28.7
$\text{HClO}_4$	DOAc	$-0.008^\circ$	0
$\text{DCI}$	Dioxane	$-6.23^\circ$	45.6

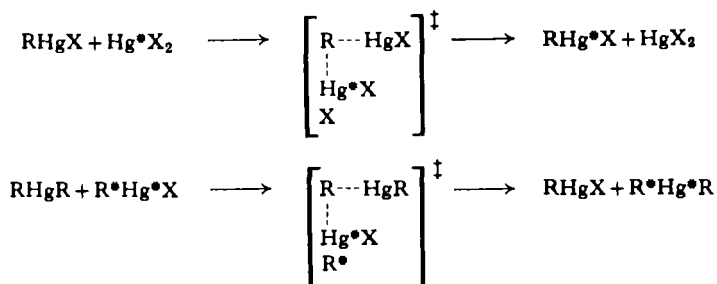
TABLE IX

ACID CLEAVAGE OF  $\text{DI}(4\text{-METHYLCYCLOHEXYL})\text{MERCURY}$

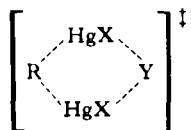
Acid	Solvent	% <i>trans</i>				
		Initial $\text{R}_2\text{Hg}$	Recovered			% Ret.
			$\text{R}_2\text{Hg}$	$\text{RHgX}$	RD	
DOAc	DOAc	100	37	37	95	—
DOAc	DOAc	18	37	37	95	—
$\text{D}_2\text{SO}_4$	Dioxane	100	41	41	95	—
$\text{D}_2\text{SO}_4$	Dioxane	16	34	31	95	—
$\text{DCI}$	Dioxane	100	99	98	80	80
$\text{DCI}$	Dioxane	18	15	14	36	73

Apparently halogen acids, which have an anion which is a good nucleophile for mercury, show high retention in the product hydrocarbon, and little rearrangement of starting material. The other systems all involve extensive racemization in recovered starting material. No mechanistic pathway has been ascribed to the racemization process.

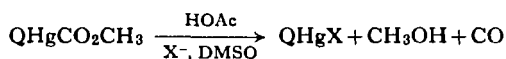
Aside from so-called two-alkyl exchange, the one- and three-alkyl exchange reaction in the organomercurial system has been studied by both radiochemical and optically active labeling experiments (129).



Good second-order kinetics, retention of configuration, and the noted tag transfer support the postulated transition states, for reactions performed in protic environments. In aprotic environments presumably nucleophilic participation at mercury would be involved.

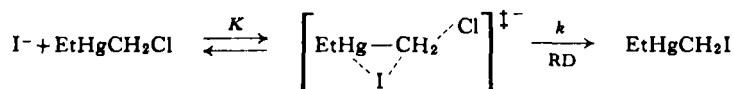


Such nucleophilic participation has been detected kinetically in the decomposition of carbomethoxymercurials.



The reaction is third order, first order in each of substrate, acid, and halide ion, the effectiveness of the added assistor decreasing in the order  $\text{I} > \text{Br} > \text{Cl}$  (130).

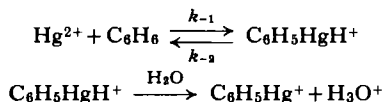
Ledwith and Phillips (131) have recently investigated the iodide substitution reaction of  $\text{RHgCH}_2\text{Cl}$  in dry and moist acetone, and report a well-behaved second-order process in anhydrous media, first order in mercurial, first order in iodide ion. The  $k_2$  values are extremely high ( $\text{BuCl} = 1$ ,  $\text{PhCH}_2\text{Cl} = 3.5 \times 10^2$ ,  $\text{CH}_3\text{COCH}_2\text{Cl} = 5.2 \times 10^4$ ,  $\text{C}_2\text{H}_5\text{HgCH}_2\text{Cl} = 1 \times 10^6$ ). In the presence of 20% water the reaction becomes first order in substrate alone, and it is suggested that



In anhydrous media  $K$  for the pre-rate-determining equilibrium is very small, but in hydrous media it is large giving rise to apparent first-order kinetics.

### G. Mercuration

Recently an excellent study has appeared on the mechanism of the mercuration of aromatic hydrocarbons (132a). These processes are strongly catalyzed by the addition of inert salts such as  $\text{NaClO}_4$ . Correlations of observed rate with physical parameters of the solution such as Hammett acidity functions fail, but the rate is inversely proportional to the activity of water in the environment, suggesting that it is the function of the perchlorate anion to aid in removal of solvating water from mercuric ion, increasing its activity in attack on the aromatic nucleus.



The large kinetic isotope effect ( $k_{\text{H}}/k_{\text{D}}$ ) suggests that deprotonation is rate-determining; in step 2, the kinetic isotope ratio is sensitive to the water concentration.

Such effects on the catalytic ability of mercuric ion by solvent water have been demonstrated in the hydration of acetylenes catalyzed by mercuric perchlorate (132b). Large amounts of water impede reaction by competing too successfully with the acetylene for coordination sites around the mercuric ion.

The important contribution by Perrin and Westheimer (132a) in this area is that it should be possible to calculate a series of  $M_0$  functions—the ability of a system to donate a metal ion to a neutral substrate—as defined by

$$\text{Hg}_0 = -\log[\text{hg}]_0 = -\log a_{\text{Hg}^{2+}} f_{\text{S}} / f_{\text{SHg}^{2+}}$$

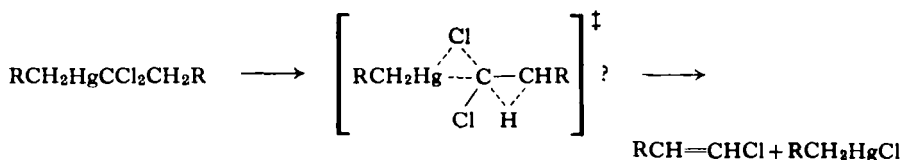
The mercuration reaction itself has been used extensively in developing the selectivity relationship, which describes the correlation between  $\log p_f/m_f$  and  $\log p_f$  where the parameters  $Q_f$  represent the partial rate factors at the indicated position. Essentially the expression  $\log p_f = k \log p_f/m_f$  indicates that the higher the reactivity a reagent possesses in attack on the substituted aromatic nucleus, the less selective it becomes. The expression is directly derivable by assuming that Hammett-like equations apply to aromatic substitutions, providing the usual substituent constant  $\sigma$  is replaced by  $\sigma^+$ , i.e.,  $\log k/k_0 = \rho\sigma^+$ .

Investigation of various mercurating species has shown that not only can the choice of mercurating reagent affect the activity of the attacking electrophile, and hence isomer distribution, but that this choice can result in

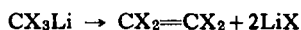
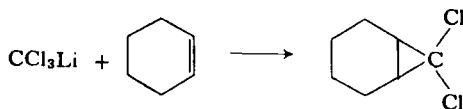
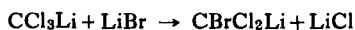
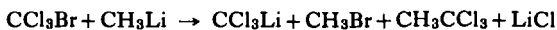
isomerizing conditions which can further alter the isomer ratio from that which might be expected on the basis of the selectivity relationship (133).

### H. Carbene Sources

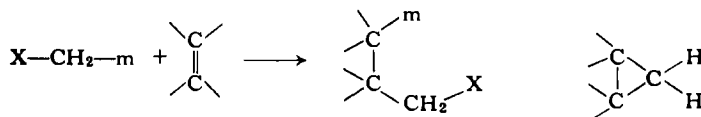
A more recent innovation is the use of polyhalomethylmercury compounds as carbene sources, or perhaps carriers (134). Treatment of  $\text{PhHgX}$  with the anions generated from base/ $\text{CHX}_3$  gives the  $\text{PhHgCX}_3$  series ( $\text{CCl}_3$ ,  $\text{CCl}_2\text{Br}$ ,  $\text{CBr}_3$ ) which on thermolysis afford dihalocarbenes ( $\text{CCl}_2$ , or  $\text{CBr}_2$ ) which will add to olefins. The compounds  $\text{CCl}_3\text{HgX}$  and  $(\text{CCl}_3)_2\text{Hg}$  are more readily available from the reaction of  $\text{NaO}_2\text{CCCl}_3$  with mercuric salts, and also undergo thermolysis in the presence of olefins to give 1,1-dihalocyclopropanes (135). These reactions involve true carbenes, since the order of reactivities of various olefins toward a given reagent is identical with that found for the  $\text{CCl}_3\text{COONa}$  route to  $\text{CCl}_2$ , and quite different from the order found for the carried carbene reagents,  $\text{XCH}_2\text{ZnX}$ , of Simmons and Smith, and from the oxymercuration sequence. The stereochemistry is one of retention of configuration of the olefin upon addition. Transfer of  $\text{CH}_2$  from  $\text{PhHgCH}_2\text{X}$  is also feasible, but not a very rapid process. These reagents may be prepared by treating  $\text{PhHgX}$  with  $\text{CH}_2\text{N}_2$  (136a, b). This latter insertion is mirrored in the reaction  $\text{R}_2\text{Hg} + \text{CCl}_2 \rightarrow \text{RCCl}_2\text{HgR}$  (136c). These compounds are unstable to heat, yielding vinyl halides and  $\text{RHgCl}$ .



The recent report (30), that  $\text{CCl}_3\text{Br}$  with  $\text{CH}_3\text{Li}$  slurry in ether at  $-115^\circ\text{C}$  affords a stable  $\text{CCl}_3\text{Li}$  species, which subsequently can react with olefins to give dichlorocyclopropanes is pertinent. The following reactions are consistent with the results:



Hoberg (31) has observed that  $\alpha$ -halomethylaluminums react with olefins to yield  $\gamma$ -halopropylaluminums, which then decompose via 1,3-elimination.



He comments that the analogous Simmons-Smith (32) reaction which also involves addition of a halomethyl metal compound across an olefin, followed by cyclization, might be similarly portrayed. Miller has pointed out, as have Goldstein and Baum (33a), that evidence against halomethylolithiums and for carbenes in the reactions introduced by Closs and Closs (34) is lacking. The question remains then as to the reality of the existence of carbenes in such organometallic cases, and whether "carried carbenes" and/or organometallic additions to olefins followed by elimination might be involved.

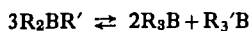
Hoeg (33c) has provided the key to this area by his observation that THF stabilizes  $\alpha$ -haloalkyl lithiums. Decomposition of these species at low temperatures is dependent on the nature and concentration of any olefin present, *not independent* as might be expected from a free carbene mechanism. Hoeg suggests a continuum of reaction structures extending from the covalent organometallic (carbanion source) through a carbene-salt complex (incipient carbene) to carbene as reaction conditions vary.

## V

### ORGANOBORON COMPOUNDS

#### A. Structural and Redistribution Problems

Although excellent work has been described (138, 139) on substitution reactions of inorganic derivatives of boron, kinetic studies are rare in the  $\text{R}_3\text{B}$  systems, primarily because of experimental difficulties centering around oxygen sensitivity, and redistribution processes presumably involving a four-center bridge intermediate



Any kinetic study involving the reaction of a b—c linkage should keep the departing group,  $\text{R}_2\text{B}$ , constant. Often this has not been done, at the cost of interpretation, to avoid redistribution. Parsons and Ritter (140) have shown

that unsymmetrical materials, relatively stable towards redistribution, may be prepared if vinyl or propenyl substituents are involved.

The  $p_\pi-p_\pi$  interaction between the vinyl grouping and the empty  $p$  orbital on boron presumably interferes with attainment of tetrahedral boron required for a bridged-intermediate mechanism. Moreover vinylboranes are weaker acids than the corresponding alkylboranes, and the reaction with molecular oxygen is sluggish. The occurrence of  $\pi$  character in c—b bonds in general has been discussed (141). Infrared spectral studies support  $\pi$  bonding in vinyl derivatives and  $B^{11}$  NMR spectra also seem to be well correlated with a theory involving vacant  $p$ -orbital occupation (142). Even in the case of trimethylboron, "hyperconjugation" has been postulated (143). It would seem that such interactions have been ignored in the Li and Mg cases, where they might also be found.

Redistribution may also be prevented by steric crowding (144), again a factor which could prevent formation of a bridged transition state (cf.  $RLi + RX$  and  $Rmg + Rhg$  exchange reactions, Section II, A). Indeed three large dissimilar groups have been placed on boron, yielding a compound stable to disproportionation, viz., *tert*-butylisobutyl-*n*-amylborane.

Considerable interest has recently been shown in the cationic organoboron complexes  $R_2B^+$  (145–148). In terms of a dissociative-type process, these are of mechanistic importance. Köster and Leffler *et al.* (148) have reported on subvalents of this series,  $R_2B$ , but characterization thus far is incomplete, and in one case, in error. Weissman has shown that alkali metal reduction of  $Ar_2BX$  yields  $Ar_3B^-$ .

### B. b—H Bond Cleavage

Borohydrides  $[BH_4^-]$  in aqueous, buffered solutions, or in diglyme, react with acids of an appropriate strength to yield  $H_2$  and b—O— products. Conceptually, this is the simplest reaction a chemist might deal with—the combination of a proton and a hydride ion—although in the present case they are primarily incipient species (149–152).

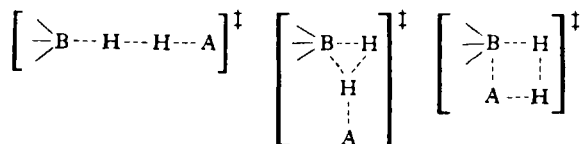
Reaction of borohydrides in aqueous systems (149) involve general acid catalysis

$$(\text{rate} = k_{H_3O}[BH_4^-][H_3O^+] + k_{H_2O}[BH_4^-][H_2O] + k_a[BH_4^-][HA])$$

At ionic strengths of 0.10,  $k_{H_3O^+} = 1 \times 10^6 M^{-1} \text{ sec}^{-1}$ . The Bronsted  $\alpha$  is nearly unity, making it rather difficult to detect the general acid terms. The most reliable data, in low pH ranges, indicates that plots of square root of



ionic strength vs.  $\log k_1$  (pseudo-first-order rate constant) are linear with a slope of  $-1$ , indicative of ions of opposite and unit charge uniting in the transition state,  $z_a z_b = (-1)(1) = -1$  (application of the Bronsted, Christiansen, Scatchard equation). Three possible transition states have been suggested for the general acid case

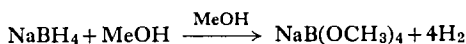
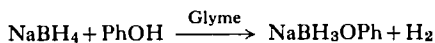


Attempts have been made to characterize the transition state and intermediates more fully. Polarography on solution of hydrolyzing borohydride reveal two species, one at  $-0.15$  V the other at  $-0.64$ , vs sce. The latter was largely ignored as an impurity until it could be trapped (153) by hydrolysis at low pH followed by quenching to high pH. A  $B^{11}$  NMR study indicated that it was a boron-containing species with three protons attached (presumably  $\text{H}_2\text{O} \cdot \text{BH}_3$  or  $\text{BH}_3\text{OH}^-$ , the latter being preferred). Isolation of only traces of  $\text{Et}_3\text{N} \cdot \text{BH}_3$  from reactions in aqueous solution between  $\text{BH}_4^-$  and  $\text{Et}_3\text{N}$ ,  $\text{Et}_3\text{NH}^+$ , has been used as an argument to exclude the four-center process. Absence of an available lone pair in the acidic component makes such a four-center process, *a priori*, unfavorable, and raises the question of identity of mechanism in the two reactions.

The  $k_H/k_D$  ratios ( $\text{BH}_4^-/\text{BD}_4^-$ ) have been measured, for the  $\text{H}_3\text{O}^+$  cleavage, yielding the remarkably low inverse isotope value of 0.7 (149, 150). Although rupture of a b—D bond is involved, a process probably yielding a  $k_H/k_D$  value greater than one, the other deuteriums not cleaving away reduces this ratio markedly. At present the assignment of actual causes to such effects seems beyond our knowledge. Briefly, observations of this type may be due to (a) vibrational effects, (b) rotational effects, (c) differential inductive effects, (d) anharmonicity effects and steric factors (154–158).

Extensive calculations (149) suggest that frequency changes on going from the ground to the transition state are the source of the inverse isotope effect but also indicate that calculated values of this parameter are very insensitive to assumed geometry, obviating this as a method of establishing a distinct transition state for the general acid case under discussion. The activation entropy for  $\text{H}_3\text{O}^+$  attack ( $-6$  kcal/mole) is *low* for a reaction of the uni-opposite charge type involved here.

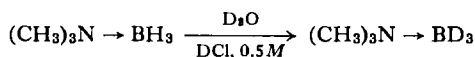
Both the reactions of phenol with borohydride, and methanol with borohydride, viz.,



have been shown to be second order in attacking acid (149, 150), suggesting the autoprotection step  $2 \text{ROH} \rightleftharpoons \text{ROH}_3^+ + \text{RO}^-$ . The former reaction also displays the same low  $k_{\text{H}}/k_{\text{D}}$  value shown by the  $\text{BH}_4^-/\text{H}_3\text{O}^+$  system, as well as a  $k_{\text{H}}/k_{\text{D}}$  ( $\text{PhOH}/\text{PhOD}$ ) of 1.7. The similarity in the  $\text{H}_3\text{O}^+$ ,  $\text{PhOH}_2^+$  and  $\text{MeOH}_2^+$  systems suggests a common type of transition state, with emphasis placed on uni-opposite charge association,  $(\text{BH}_4^-, \text{ROH}_2^+)$ , and low activation energy, correlated with a negative activation entropy indicative of a highly ordered transition state. The most reasonable transition state is the four-center one, where coordination of oxygen with the boron weakens the b—H bond, concomitant with activation of the O—H linkage, making the incipient proton a better electrophile. The exact timing of the processes involved in  $\text{H}_2$  production is unknown. One interesting outcome of this study is the report (149) that this mechanistic scheme involving  $\text{MeOH}_2^+$  adequately explains the fact that  $\text{NaBH}_4$  has become “more stable” in methanol. Early samples of the material were impure and repressed autoprotection of the methanol.

In 1961 Jolly (152) reported the fact that  $\text{BH}_4^-$  exchanges its incipient hydride ions with deuterium in the solvent pool by two different pathways, one pH-independent, and measurable at very high pH's, while the other path is catalyzed by acid and occurs in solutions undergoing hydrolysis at ordinary temperatures. The activation energy for exchange is less than that for hydrolysis. It has been reported (159, 160) that micromolar amounts of metal ion can catalyze this exchange process and the former observations may have to be re-examined.

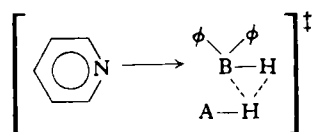
An associated reaction



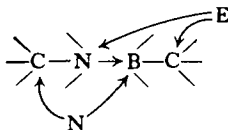
suggests the incorporation of deuterium in organic molecules via subsequent hydroboration (161).

Vexing problems on transition state structure have also been promulgated by work on hydrolysis of amine-boranes (162–164).

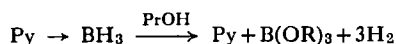
Hawthorne and Lewis (162) have investigated the hydrolysis of  $\text{Py} \rightarrow \text{BPh}_2\text{H}$  by water in acetonitrile. The reaction obeys the kinetic law, rate =  $k_2[\text{Py} \rightarrow \text{BPh}_2\text{H}][\text{HOH}]$ , with a Hammett  $\rho$   $[(\text{Z}-\text{C}_6\text{H}_4-)_2\text{BH}]$  of 0.76. The  $k_{\text{H}}/k_{\text{D}}$  values are  $\text{b-H/b-D} = 1.5$  and  $\text{HOH/DOD} = 6.90$ . Somewhat better estimates for these ratios appear to be available from later work (163), values of 1.4 and 6.04, respectively, being reported. In this study  $k_{\text{H}}/k_{\text{T}}$  values of 1.77 and 12.4 were found. Studies on the temperature dependence of the isotope effects indicate that the entire isotope effect arising from substitution in the water molecule can be adequately explained by assuming that most of the zero-point energy of the O—H stretch is lost in the transition state. On the other hand, the  $\text{b-H/b-D}$  isotope effect is independent of temperature, the source of the isotope effect being in the pre-exponential factor of the Arrhenius equation. Values of 1.4 and 1.7 for the deuterium and tritium substitutions are close to the  $(2)^{1/2}$  and  $(3)^{1/2}$  values predicted by applying the Bigeleisen, Wolfsburg treatment, which predicts that in certain simplifications of the general equation for isotope effects the square root of the reduced mass of the system undergoing the imaginary vibration in passing across the transition barrier will appear in the pre-exponential term. These studies are consistent with the transition state in which the borane hydrogen is not firmly bound, but the water hydrogen is. A three-center model, with or without oxygen participation at boron is compatible with the data.



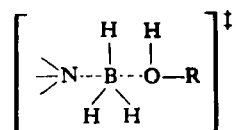
Ryschkewitsch (164) has elegantly pointed out that in electrophile/nucleophile attack on amine-boranes, the following positions of attack may be involved:



He has studied the solvolysis of  $\text{Py} \rightarrow \text{BH}_3$  with propanol in alcohol, and alcohol/water mixtures.



The rate is first order in borane, and linear plots of  $\log k$  vs.  $(D-1)/2(D+1)$  with negative slope suggest that charge dispersal is involved in reaching the transition state. Pyridine in solution does not retard rate, and the introduction of substituents on the pyridine ring shows that those which render the N more basic retard the rate (+  $\rho$  value). These results are consistent with a mechanism which involves dissociation of the  $\text{>N} \rightarrow \text{b}$  link in the rate-determining step. Since activation energies for this process are lower than the dissociation enthalpies for the process  $\text{Py} \rightarrow \text{BH}_3(\text{gas}) \rightarrow \text{Py} + 1/2 \text{B}_2\text{H}_6$ , this suggests solvent participation

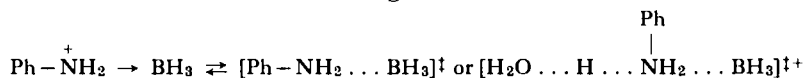


leading to displacement of pyridine, and production of  $\text{BH}_3$ , which decomposes rapidly.

Study of the hydrolysis of substituted aniline-boranes in dioxane-water indicates (165) the reaction is first order in borane, and that there is a pH-dependent as well as a pH-independent path

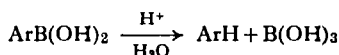
$$\{\text{rate} = [p\text{-XC}_6\text{H}_4\text{NH}_2 \cdot \text{BH}_3] (k + k'[\text{H}_3\text{O}^+])\}$$

The ratio  $k/k'$  varies from 1 ( $\text{X} = \text{Cl}$ ) to 0.1 ( $\text{X} = \text{CH}_3\text{O}$ ). The pH-independent rate is enhanced by electron withdrawal, while the pH-dependent rate is suppressed. The  $\rho$  values are +2.3 and -1.3, respectively. There is no isotope effect ( $\text{BD}_3$ ), and for the *p*-toluidine case activation energies are about 20 kcal/mole, and activation entropies near zero for both mechanisms. *N*-Alkyl substitution aids the pH-independent process and retards the other mechanism. No inhibition by added aniline is found. The data are consistent with the following transition states:



### C. *b*-R Bond Cleavage

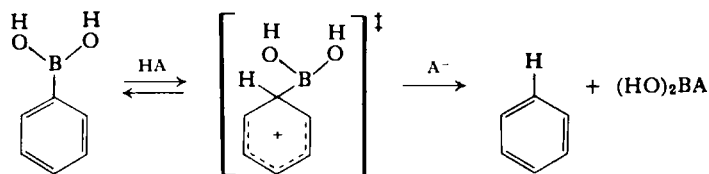
Carbon-boron cleavages involving acid-catalyzed protodeboronation of areneboronic acids have been examined (166).



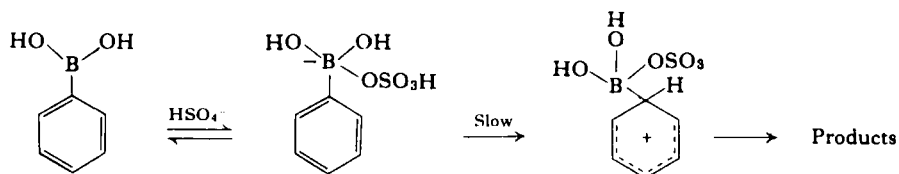
The acid-catalyzed process, employing methoxyphenylboronic acids as substrates in concentrated sulfuric or perchloric acids indicates that the observed pseudo-first-order rate constant follows the Hammett-Zucker correlation of  $\log k$  vs.  $H_0$ . The latter represents the ability of a solution to donate a proton to a neutral substrate, a proclivity measured by  $[BH^+]/[B]$  ratios in the system, where B is an indicator related in structure (hopefully) to the substrate (S) in question. The basis for this equation has been discussed (167). Normally such correlations have been used as evidence for an A-1 mechanism, involving pre-equilibrium proton transfer to substrate, followed by unimolecular decomposition of the complex. However rate-determining protonation of substrate (A-S<sub>E</sub>2 mechanism) may also give a Zucker-Hammett correlation (167). Conceptually one asks: In the transition state is the proton transfer just beginning (when the excited state resembles reactants), thus allowing the rate to follow  $H_3O^+$ , or is transfer virtually complete (with the transition state resembling products), allowing a comparison with the A-1 mechanism which permits the rate to follow  $H_0$ ? In the present case, in phosphoric acid solutions, methoxyphenylboronic acid shows a linear  $\log k$  vs.  $H_0$  plot with slope of 1.85, while theory predicts a slope of unity. In *dilute* solutions, studies with phosphoric acid buffers definitely show a term due to  $H_3PO_4$  in the rate law, suggesting that an A-1 mechanism may be eliminated, and that one is dealing with general acid catalysis. This is confirmed by later work on malonate/malonic acid systems where plots of  $\log k$  vs. pH show a distinct minimum at pH 4.8, while at pH 3.6 the rate is proportional to malonic acid concentration from the added buffer. Of the mechanisms remaining there are A-S<sub>E</sub>2, rate-determining proton transfer from acid to substrate; A-2, pre-equilibrium proton transfer followed by rate-determining conjugate base attack; rA-2, the reverse of A-2; or multicenter, pre-equilibrium formation of complex  $HA \rightarrow B(Ar)(OH)_2$  followed by rate-determining intramolecular proton transfer. Pruning may be accomplished by using Gross-Butler equations (168), with certain modifications (169).

Knowing rate data in pure  $H_2O$  and  $D_2O$ , having available thermodynamic data on lyonium ion acidities, and by assuming the Bronsted catalysis law, it is an easy matter to calculate rates in mixed solvents based on (a) proton transfer as a rate-determining step, or (b) pre-equilibrium proton transfer. The present system adheres to rate-determining proton transfer, and thus A-2 mechanisms are eliminated. The agreement between theory and experimental values suggests that special features

of the phosphate anion need not be invoked, and that the reaction is A-S<sub>E</sub>2.



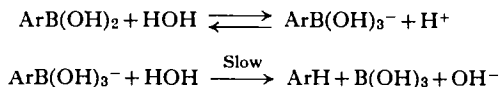
However, when the substrate is changed to one containing a more electron-withdrawing group, anion participation seems to be involved. Plots of  $\log k$  vs.  $H_0$  in the sulfuric acid cleavage of various boronic acids ( $Z = m\text{-Cl}$ ,  $m\text{-NO}_2$ ,  $m\text{-F}$ ,  $p\text{-CH}_3$ ) show distinct breaks in slope. At high acid concentrations the A-S<sub>E</sub>2 process is still involved, but at lower concentrations the multicenter mechanism is important,



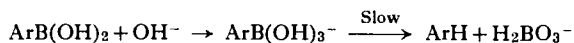
The rationale would presumably involve the following thought processes. Methoxyboronic acids have a low acidity, and thus are unlikely to involve  $\text{HA} \rightarrow \text{B}$  interactions. They also have the highest electron density on the susceptible carbon, promoting electrophilic proton attack. As the substituents withdraw density from the c—b area, the boron becomes more acidic, and prone to coordination with nucleophilic portions of the attacking acid, while the carbon atom in question becomes more difficult to attack. The route of direct electrophilic attack on carbon becomes a high-energy step, and the four-center route is favored. The coordination step not only increases the susceptibility of the adjacent carbon to attack, by increasing the electron density at that position, but also results in an increased ability to transfer a proton. As expected, the price one pays for invoking this pathway is in terms of entropy. In 30% sulfuric acid, when the substrate is changed from *p*-methoxybenzeneboronic acid to *p*-tolueneboronic acid, the rate is decreased by 2.5 powers of 10, reflected by a drop of 10 activation entropy units.

There also appears to be a base-catalyzed and pH-independent reaction

of the boronic acids. When *o*-methoxybenzeneboronic acid reacts with malonic acid/malonnate buffer, the linear relationship observed between pH and  $\log k_{\text{obs}}$  with unit slope suggests, for the region pH 6.0–6.7,

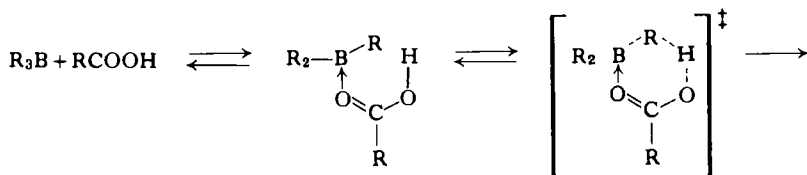


or



Although the acid-catalyzed reaction gave a Hammett plot with  $\sigma^+$  values with a  $\rho$  of  $-5.0$  (pure  $\text{A-S}_{\text{E}}2$  process), the present case correlates best with  $\sigma$  values giving a  $\rho$  of  $-2.3$ . To be discussed later are the corresponding  $\rho$  values for the cleavage of  $\text{C}_6\text{H}_5$ -*m* linkages with acids as follows: (*m*,  $\rho$ ; Si,  $-5.0$ ; Ge,  $-4.6$ ; Sn,  $-3.8$ ; Pb,  $-2.5$ ; Hg,  $-2.8$ .) A low  $\rho$  value in electrophilic substitution is attributed to some means of reducing electron demand on substituents by the seat of reaction; in this case it is the boronate anion which is reacting.

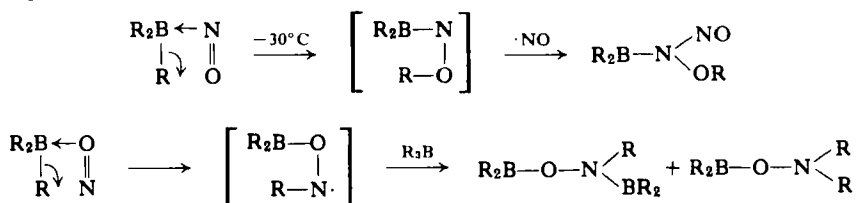
All of these conclusions are in agreement with observations (170*a*) on the cleavage of triethylboron in glyme by substituted benzoic and acetic acids. The reaction is first order in each, and plots of  $\log k$  vs.  $\text{pK}_{\text{a}}$  gives a positive slope, such that the *stronger acids react less rapidly*. Addition of DMSO retards the rate, while addition of methyl acetate or trifluoroacetic acid do not affect the rate of reaction. These data, coupled with an isotope effect  $[\text{RCOOH}/\text{RCOOD}] k_{\text{H}}/k_{\text{D}} = 2$ , are suggestive of the mechanism



Again coordination of the boron with the carboxylic acid nucleophile activates the R group for cleavage, and labilizes the proton that is involved in rate-determining attack. In agreement with this concept very weak acids, with properly placed nucleophiles, react with triethylboron, e.g., 1,3-diketones, acetamide, 2-pyridone, pyrrolidone, and 8-hydroxyquinoline.

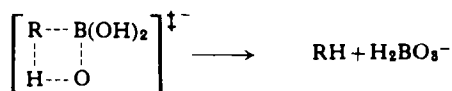
A recent re-examination of the reaction of triethylborane with nitric oxide

has revealed that two pathways are open, the choice being temperature-dependent,

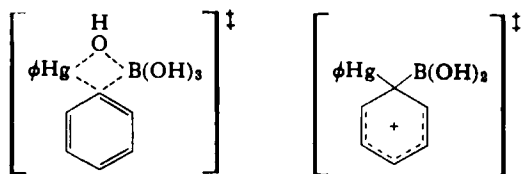


A four-center attack by the electrophile/nucleophile (170*b*) pair is proposed.

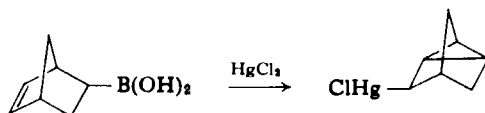
Since base-catalyzed cleavage of the hydroboration products of *cis*- and *trans*- $\alpha, \alpha'$ -dimethylstilbene gives *meso* and *dl* hydrocarbon, respectively, this has been taken as evidence for a four-center process.



Metallodeboronation of phenylboronic acids has been also studied (171). Phenylmercurideboronation of benzeneboronic acid in aqueous ethanol using phosphate buffers, yields equilibria  $\text{PhHgX} \rightleftharpoons \text{PhHgOH} \rightleftharpoons \text{PhHg}^+$  and  $\text{PhB}(\text{OH})_2 \rightleftharpoons \text{PhB}(\text{OH})_3^-$ , suggesting two possible transition states for this process



Matteson (172) has recently reported that for

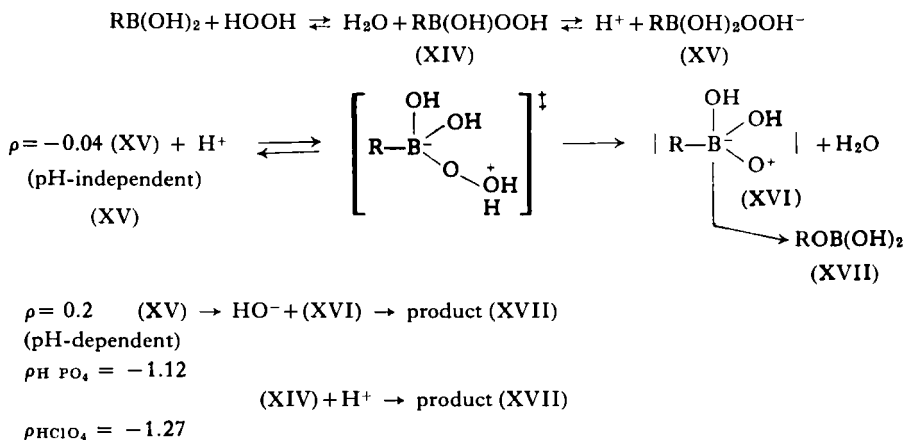


$k_{\text{exo}}/k_{\text{endo}} \geq 100$ , while  $\text{B}^{10}/\text{B}^{11}$  isotope effect studies indicate that the c—b bond is rupturing in the rate-determining step. The author assumes transannular displacement, with considerable precedence for such a process. The stereochemistry of mercurideboronation is being explored (172).

An even more complex mechanistic jungle appears in the peroxide cleavage of boronic acids (173, 174). Kuivila and his co-workers have again



done the pioneer work. There are acid- and base-catalyzed processes, as well as a pH-independent process. Specific acids (sulfuric, perchloric, and phosphoric acids) appear to have different mechanistic routes open to them. All of these processes are first order in peroxide and boronic acid. The base-catalyzed process exhibits a term first order in  $(\text{OH}^-)$ , while the phosphoric acid-catalyzed process follows  $H_0$ , and the rate constants are also proportional to the ratio  $a_{\text{H}_3\text{PO}_4}/a_{\text{HOH}}$ . With perchloric acid or sulfuric acid  $H_0$  is not followed, and the activity correlation is  $k_{\text{HClO}_4} \propto (a_{\text{HOH}})(a_{\text{HClO}_4})^{1/2}$  and  $k_{\text{H}_2\text{SO}_4} = (a_{\text{HOH}} \cdot a_{\text{H}_2\text{SO}_4})^{1/2}$ . Suggested mechanisms and transition states are:



Low  $\rho$  values suggest that electromeric release is not brought into play to any extent during the slow step.

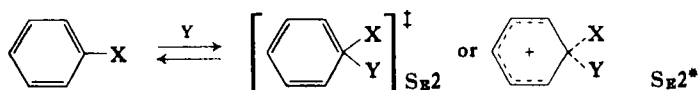
In the pH-dependent case the rate-determining step appears to be scission of the O—O linkage since the *p*-MeO group fits the Hammett correlation. In electrophilic substitution situations it would normally require  $\sigma^+$  values.

In the other cases it is more difficult to assign transition states, but it is obvious that the mechanistic picture is sensitive both to reagent and substrate.

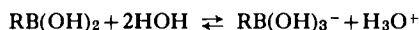
The basic mechanism has been clarified by labeling as follows:  $\text{RB(OH)}_2 + \text{H}_2\text{O}^{18} + \text{HOOH} \rightarrow \text{R}^*\text{OH}$  with retention of configuration and no incorporation of label (175).

Traylor and co-workers (174) prefer to distinguish two separate cases of displacement at a c—m bond. One of these is  $\text{S}_{\text{E}}2$ , where the two electrophiles are attached to the carbon orbital without appreciable rehybridization

or development of charge on carbon, while the  $S_E2^*$  notation is reserved for those cases in which an intermediate of the Pfeifer-Wizinger type (176) is involved. The near zero values above are compatible with  $S_E2$  character in these processes.



As mentioned, three processes are involved in these reactions—attachment of the peroxy group, loss of hydroxide moiety by O—O scission, and transfer of the R group. Traylor *et al.* have attempted to separate the effects of the pre-rate-determining coordination from the rest by establishing  $K_a$  for the reaction



justifiably assuming  $K_a^{\text{HOH}} \propto K_a^{\text{HOOH}}$ . Table X illustrates the data.

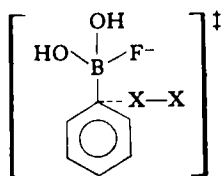
TABLE X  
BORONIC ACID CLEAVAGE PROCESSES

$\text{RB(OH)}_2 \xrightarrow{\text{HOOH}} \text{ROB(OH)}_2$ $\text{RB(OX)}_2 + 2\text{H}_2\text{O} \xrightleftharpoons{K_a} \text{RB(OH)}_2^- + \text{H}_3\text{O}^+$					
R	$k_2$ ( $\text{M}^{-1} \text{sec}^{-1}$ ) $H_0 = 5.23$	$k_2'$ ( $\text{M}^{-1} \text{sec}^{-1}$ ) $H_0 = 1.48$	$K_a$	$k_2/K_a$ (rel.)	$k_2'/K_a$ (rel.)
Me	0.00013	0.00024	2.5	(1)	(1)
<i>n</i> -Bu	0.0048	0.0072	1.8	52	42
<i>sec</i> -Bu	0.023	—	2.5	185	—
<i>tert</i> -Bu	0.072	0.094	4.3	330	229
$\phi$	0.016	0.032	138	2.3	—
$\text{CH}_2=\text{CH}-$	0.0068	—	32	4.2	2.4
$\phi\text{CH}_2$	0.088	—	73	24	—

It is assumed (174) that R migrates with considerable carbanionic character and that the series represents the electronic sequence for the  $S_E2$

reaction. The data would equally fit either a process involving development of carbonium ion character in the migrating group, or a mechanism in which peroxide link cleavage was the predominant energy-determining step. The former has an analogy in the Baeyer-Villiger rearrangement. The fact that the sequence arrived at is in disparity with the series developed by M-H, M-M, and M-X interchange reactions, and cleavage of c—hg bonds by acids, where electrophilic attack has been also emphasized, indicates much further work is needed. A similar reaction is known in the silicon system and here in mixed compounds  $\text{Me}_2\text{PhSiOOR}$ , only Ph migrates (177).

The related direct oxidation of trialkylboranes has been studied (178), as well as the brominolysis and iodinolysis of benzeneboronic acid in aqueous acetic acid (50%) and *m*-chlorobenzeneboronic acid in aqueous solution. The latter reveals a pattern involving tetravalent boron (179). In water solutions, and acetate buffers at constant ionic strength with the *m*-chloro derivative, plots of  $\log k$  vs. pH were linear with unit slope (from pH 2 to 5), suggesting specific lyate ion catalysis. In both cases catalysis by fluoride ion was observable, and catalysis by hydroxy acids or diols, which form coordination complexes with boron, was seen in the latter case. Indeed in water solvent, the catalytic constant for fluoride ion is some 6000 times that of the uncatalyzed case.



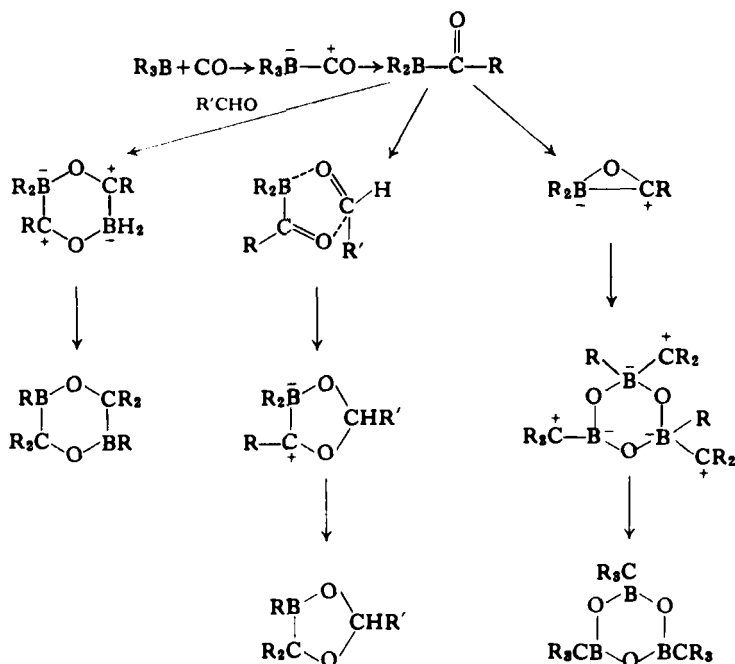
It must be concluded that this is another example of nucleophilic assistance. In this case even in protic environments the fluoride ion can serve as this agent, presumably because of the hard/hard nature of the interaction. We shall see that in the R—sn system, hydrogen-bonding solvents wash out such nucleophilic participation from the observed kinetics.

#### D. Addition Reaction

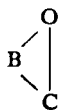
Boron-hydrogen bonds undergo addition to double bonds readily. The well-known hydroboration reaction has been extensively studied and thoroughly reviewed (180). It involves a *cis* addition of b—H to the  $\text{C}=\text{C}$

linkage, in the Markownikoff direction. Another important preparative reaction of this type is the reduction of ketones by borohydride ion. This reaction has been studied kinetically and stereochemically (181-189); it will not be treated in detail since it lies outside the scope of this article.

Addition reactions of trialkylboron compounds are few, for the R—b linkage does not add to conventional C=O or C=C bonds. Trialkylboranes will, however, undergo carbonylation by carbon monoxide.



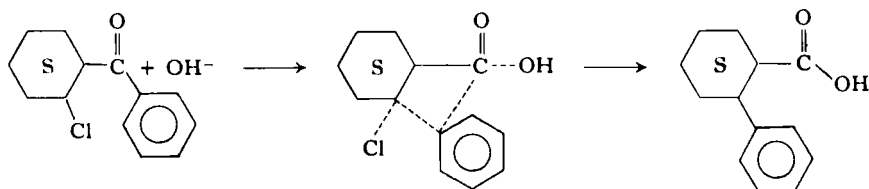
The postulated explanations involving 1,3-dipolar addition and the formation of a



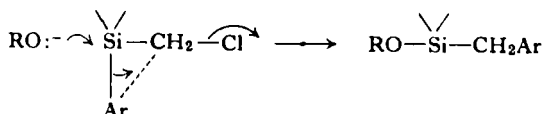
ring system seem provoking enough to merit inclusion here (190). One other addition reaction of organoboranes which is being studied mechanistically is the reductive alkylation of quinones (191).



Transfer of the organic ligand is to be noted, and the fact that ethyl group is sluggish contrasts with what is found in Traylor's series, which is superficially analogous. The processes are analogous to the Stevens reaction (194, 195)



and



## VI

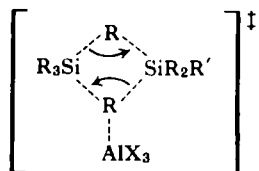
### ORGANOSILICON AND ORGANOTIN COMPOUNDS

As mentioned in the Introduction, this section will include only data related to displacements at silicon involving carbon or hydrogen. The stereochemistry of displacements involving halogen, alkoxy groups, and ester functions has been explored by Sommer and his co-workers (196). Similar studies with germanium have been carried out by Brook (197).

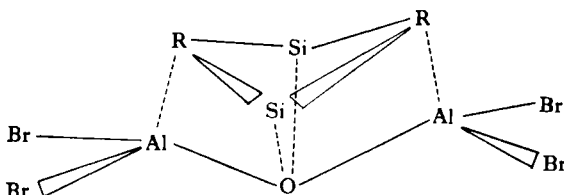
#### A. Redistribution Reactions

Unsymmetrical organosilicon compounds are quite stable, and the mechanism of disproportionation of a typical member of the family ( $\text{EtMe}_3\text{Si}$ ) has been investigated (198) with Lewis acid catalysis ( $\text{AlBr}_3$ ). Because carbonium ion traps do not impede the reaction,  $\text{R}_2\text{AlCl}$  is a better catalyst than  $\text{R}_3\text{Al}$ , and moreover because silylation products are not observed, it has been concluded that carbonium ions ( $\text{R}^+$ ), organoaluminum transfer species, and siliconium ion intermediates are not involved. Important features of the reaction are that it is not autocatalytic, has an extremely low *PZ* factor, is first order in  $\text{AlBr}_3$  and  $3/2$  order in silane. Traces of many polar materials accelerate the reaction, but large amounts destroy catalyst

activity. Furthermore hydrogen and phenyl groups migrate more readily than alkyl groups. To account for these facts, Russell (199) has proposed



The accelerating effect of materials capable of forming species such as  $\text{Br}_2\text{AlOAlBr}_2$  is attributed to bridge structures, such as



The initial rates of disproportionation of a number of alkyltrimethylsilanes in benzene have been measured. Relative rates, along with comparative figures for a nucleophilic substitution at the same center are given in Table XI. The similarity is obvious.

TABLE XI

COMPARISON OF RATES OF DISPROPORTION OF  $\text{RSiMe}_3$  AND  
NUCLEOPHILIC SUBSTITUTION OF  $\text{RX}$

R	Disproportionation of $\text{RSiMe}_3$	Rate of iodide exchange
Allyl	71	42
Ethyl	1	1
<i>n</i> -Propyl	0.61	0.63
Isopropyl	0.0048	0.038
Cyclopentyl	0.059	0.046
Cyclohexyl	0.0021	0.000007

Both a base-catalyzed (200) and a radical process (201) for redistribution have been reported, but not investigated; the latter involves a silyl radical chain carrier.

The analogous processes in the Ge, Sn, and Pb cases is not as well documented although considerable industrial data certainly exist.

### B. Radical and Anionic Species

Data on the formation of trialkylsilyl radical can be obtained from Russell's data (Table XII) on chain transfer constants for various solvents in styrene polymerization.

TABLE XII  
STYRENE POLYMERIZATION CHAIN TRANSFER CONSTANTS

Solvent	Chain transfer constant $\times 10^5$ (60°C)
Benzene	0.15
Toluene	1.25
Ethylbenzene	6.7
Diphenylmethane	23
Triphenylmethane	35
Triethylsilane	22
Triphenylsilane	300

This constant would appear to be related to the strength of the Si—H bond, but the contributions to this measurement by both activation energies and frequency factors preclude an assignment of resonance stabilization energy to the silyl radical (206).

Evidence would seem to indicate a high degree of instability for the radical and a low degree of delocalization compared with  $\text{Ph}_3\text{C}$ .

The  $\text{R}_3\text{M}^-$  ions have been fairly well studied, and for the Group IV metals relative proton affinities suggest the acidity  $\text{Ph}_3\text{SnH} > \text{Ph}_3\text{GeH} > \text{Ph}_3\text{SiH}$  with  $\text{Ph}_3\text{SiH}$  lying between  $\text{PhCH}_3$  and  $\text{Ph}_2\text{CH}_2$  (207). Although an example of the elusive siliconium ion, the triphenyl(bipyridyl)siliconium ion, has been prepared (202a), this compound, of course, possesses a five-coordinate Si with a partial negative charge, and therefore the quest will undoubtedly continue for an authentic siliconium ion intermediate. The nature of  $\text{R}_3\text{Sn}^+$  species in the crystalline state, and in solution has been the subject of much discussion (202b–e).



Early reports (203a) of the successful trapping of the other *bete noire* of silicon chemistry, the substituted silene, were partially incorrect. In an attempt to obtain silene derivatives the thermolysis of polydimethylsilanes, and the reaction of  $\text{Me}_2\text{SiCl}_2$  with sodium, in the presence of toluene were studied. The products were subsequently identified as 1,4-disilacyclohexadiene derivatives (203b, c), not silacyclopropenes as originally suggested. Skell (204) has suggested that the gas-phase reaction of  $(\text{CH}_3)_2\text{SiCl}_2$  with sodium in the presence of  $(\text{CH}_3)_3\text{SiH}$  yields pentamethyldisilane via silene insertion into  $\text{Si}-\text{H}$ . The observations suggest a singlet state for the species; spin conservation rules require that triplet silene react with trimethylsilane to produce two monoradicals for which geminate coupling is precluded. The decomposition of the dimethylsilene to  $\text{CH}_3-\text{SiH}=\text{CH}_2$  is precluded by the inability of silicon to  $p_\pi-p_\pi$  double bond to carbon.

The chemistry of divalent tin has been reviewed (205a-c). Divalent lead species are currently being re-examined by Van der Kerk (205d).

### C. $\text{C}-m$ Bond Cleavage

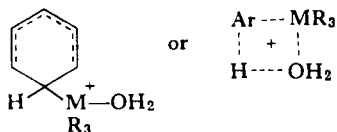
The protodesilylation (208, 209) reaction has been exhaustively explored, and at this point there appears to be merit in considering related data involving germanium, tin, and lead compounds.

Although it is difficult because of the large rate spread to measure the rates of reaction of a series  $\text{R}_3\text{MR}'$  with the same solvent(s) and acid (HA), overlap techniques assure us that in solvents where donor activity is minimal, the protolysis of  $\text{PhMEt}_3$  follows the order  $\text{M} = \text{Si}, 1; \text{Ge}, 36; \text{Sn}, 3.5 \times 10^5; \text{Pb}, 2 \times 10^8$ . The negative rho values appear to drop in magnitude as one descends the table. Use of the modified Hammett equation,  $\log k/k_0 = \rho[\sigma + r(\sigma^+ - \sigma)]$  (210) indicate that the value of  $r$  also drops monotonically (Si, 0.7; Ge, 0.65; Sn, 0.4) for cleavage in the  $(\text{C}_6\text{H}_{11})_3\text{MC}_6\text{H}_5$  series. In this equation the familiar Hammett functions are employed with the addition of  $r$ , a variable which can be altered to mix normal sigma constants and electrophilic substitution sigma constants to fit a particular case. Its function may best be seen by permitting it to have two limiting values, 0, for little charge developed on the attacked carbon, and 1, where a large partial positive charge seems to be developed on the attacked carbon.

These sequences are related to the increased availability of  $d$  orbitals on the metals as one descends the table, and appear to be related to bond

strength (Si, 60; Sn, 54; Pb, 31 kcal mole<sup>-1</sup>) but do not correlate well with estimated electronegativities (211).

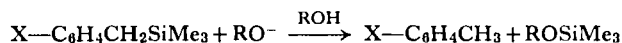
The following types of transition states are presently favored:



Indeed, in certain systems the rates follow the Hammett acidity function (212).

The fact that silyl compounds appear to be least involved with solvent has been utilized by both Eaborn and Benkeser in evaluating the electrical effects at a particular position in a substituted benzene ring. The rate of the protodesilylation reaction at that point is a measure of the ability of the substituting group to provide electron density at the point of attachment of the silyl group. In this manner polycyclic, heterocyclic, and disubstituted ring systems have been studied.

The base-catalyzed solvolysis of organosilanes (213, 214)



shows a positive rho value, and good correlation with  $\sigma$ . No data capable of distinguishing between an S<sub>N</sub>2 displacement and a quinquivalent silicon intermediate appear to exist. Much information is available for this reaction, and is excellently summarized in Eaborn's text (215). The data involve such unknown and variable conditions that mechanistic interpretation is not merited.

In passing, however, it is worth mentioning that results suggest that for derivatives of Groups IV and Ib, and III that electrophilic cleavage of phenyl and vinyl groups will be easier than cleavage of alkyl groups (barring pentafluorophenyl derivatives in which electron density at the attacked carbon is low), in contrast to what is true for Group I-II derivatives. Care must be exercised in defining a universal sequence since specific phenyl(or vinyl)-M interaction can occur, and cleavage of alkyl groups from mercury by electrophilic reagents has yielded two sequences for the classical Me, Et, iso-Pr, *tert*-Bu sequence. A qualitative picture of group cleavage in the tin series has been presented (216), but the conditions of all experiments were not identical, a situation shared by all other electrophilic cleavage sequences.

The major amount of controlled work has been done by Gielen and Nasielski (217), providing a pathway for understanding  $S_E$  reactions. Unfortunately throughout their studies they employed symmetrical species,  $R_4Sn$ , so that the leaving group is always changing. This must be kept in mind in discussing their work.

Table XIII correlates their data with those of other workers on cleavage of  $R-sn$  or  $R-hg$  bonds.

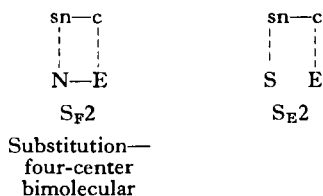
TABLE XIII  
R—SN AND R—HG BOND CLEAVAGE

		R—hg + E—N → RE + hg—N			
E—N:		$R_2Hg$	$RHgI$	$R_2Hg$	
Solvent:		HCl	$HClO_4$	$HgBr_2$	
		Dioxane	HOAc	EtOH	
R = Me		100	100	100	
Et		770	44	42	
n-Pr		460	22	—	
iso-Pr		510	13	—	

		$R_4Sn + E—N \rightarrow RE + sn—N$						
E—N:		$I_2$	$Br_2$	$Br_2$	HCl	$I_2$	$I_2$	$Br_2$
Solvent:		PhCl	PhCl	$CCl_4$	$C_6H_6$	MeOH	AcOH	DMF
								AcOH
R = Me		100	100	100	100	100	100	100
Et		600	1200	9300	750	12	37	46
n-Pr		78	450	4500	300	1.5	4.3	66
iso-Pr		560	1300	80000	300	—	—	2.5

Their interpretation is that in the extreme case two separate mechanistic pathways are open, and variations in observed sequence of alkyl groups are due to the relative contribution of each to the actual transition state. These extremes are those mentioned in the introduction,



They have attempted to correlate the ability of solvent to serve as a nucleophilic assistor or catalyst for the process using a two-parameter equation,  $\log k/k_0 = pX$ . This is similar in form to the Grunwald-Winstein equation ( $\log k/k_0 = mY$ ) developed for solvent participation in nucleophilic substitutions, where the electrophile character of the media was correlated. The parallel with the Swain four-term equation is obvious. Some attempt at placing this assessment of nucleophilic character on a more directly observable basis has been made by measuring  $J_{\text{Sn}^{117}\text{-H}}$  coupling constants for  $\text{Me}_3\text{SnH}$  in the various solvents. The feeling is that this is leading to the correct approach, and that further experiments with constant leaving group will solve this perplexing problem.

Pertinent is the recent report that fluoride ion catalyzes the ethanolysis of  $\text{C}_6\text{F}_5\text{sn}$  compounds, as well as  $\text{C}_6\text{F}_5\text{b}$  (217*g*). Literature reports of uncatalyzed  $\text{CF}_3\text{hg}$  hydrolysis suggest all of these are due to the large I effect of  $\text{R}_\text{F}$  opening up a pathway predominantly involving nucleophilic attack.

#### D. *m*—H Bond Cleavage

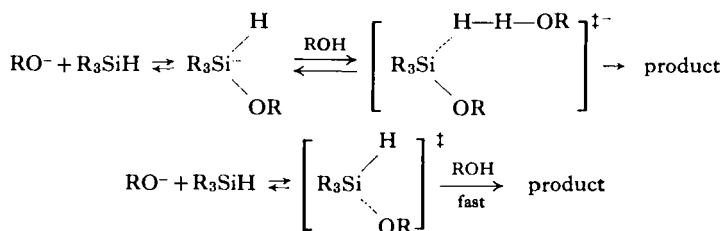
Both acid- and base-catalyzed cleavage of  $\text{si-H}$  bonds has been studied (218–222).

In base-catalyzed solvolysis studies, the stage was set by Price's work on  $\text{KOH/EtOH}$ ,  $\text{HOH}$  cleavage of trialkylsilanes. The reaction is first order in silane, and first order in base. As water concentration is varied, the plots of  $\log k_{\text{obs}}$  vs.  $[\text{HOH}]$  suggest that a molecule of water can be tied up in the transition state, although later work suggests that this observation is related to changes in  $[\text{OH}^-]$  by a medium effect. Eaborn has also pointed out that the cation of the base affects the rate and that added  $\text{LiClO}_4$  impedes reaction.

Although it is reported (223) that the reaction on solid  $\text{KOH}$  goes with retention, the stereochemical pathway in homogeneous reactions remains unknown. Attempts to perform such experiments would, according to the reported data, lead to racemization of product before isolation could be achieved. However, the fact that bridgehead silicon hydrides react more rapidly than open-chain counterparts suggests that frontside attack is involved (224).

Since solvolysis of  $\text{X-PhPh}_2\text{SiH}$  in moist piperidine gives a good Hammett correlation, with positive  $\rho$ , and isotope studies in  $\text{Ph}_3\text{SiH/}$  aqueous piperidine, and  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{H}_2\text{O}$ ,  $\text{KOH}$  involving both solvent and

substrate show the expected primary isotope effects, the following pathways are possibilities:



The value for the Si—H isotope effect is near that to be expected for a transition state with considerable H—H bonding. This has been used as an argument for a transition state resembling product, but this would not seem to stand the scrutiny of more recent interpretations of isotope effects (225).

Steward has shown that cleavages of substituted trialkylsilanes in ethanol by hydroxide ion have a Taft plot ( $\log k/k_0 = \rho\sigma^*$ ) which correlates best with two straight lines rather than one and has a large positive  $\rho$ . In the past the resulting concave upward curve has been attributed (226) to a gradual change in mechanism as the substituents are modified. The suggestion seems to be made that as the substituents are made more electron-donating, thus rendering the quinquicovalent silicon intermediate less stable, attack on hydride becomes increasingly important in energetic considerations. As might be expected, this shift in emphasis from nucleophilic attack to electrophile/nucleophile attack results in a decrease in  $\rho$ . Similar decreases in  $\rho$  have been observed in acid cleavages of the C—Si, Ge, Sn, and Pb sequence, additions of Grignards to Schiff bases, and in the boronic acid cleavages, in fact, wherever simultaneous electrophile/nucleophile attack has been postulated.

In aqueous ethanol acid-catalyzed solvolysis of triorganosilanes is first order in silane and in oxonium ion. Extensive studies on alkyl derivatives indicate that the Taft equation is obeyed with a small positive  $\rho$  value (227–229). Reaction is very slow in anhydrous dioxane, but is accelerated by water even though the indicator acidity rises, suggesting that in addition to oxonium ion another nucleophile is important somewhere during or before the rate-determining process. In higher acid concentrations the rate increases more rapidly than might be expected, and the possibility that molecular HCl or chloride ion nucleophile may be involved has been suggested. Taketa has claimed evidence for kinetic terms in oxonium ion and chloride ion in anhydrous ethanolic HCl environments. The problem is

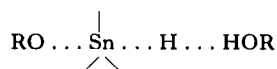
confused by lack of exact knowledge concerning acid species in such solvent systems, and at present it seems best to regard the data as being consistent with a transition state involving concerted electrophile–nucleophile attack.

Reaction between  $R_3SiH$  compounds and iodine has been investigated but the results are very complex (230a).

Other reactions suggestive of electrophile–nucleophile attack character include triethylsilane not reacting with ammonia alone, but doing so in the presence of trace amounts of sodamide (230b) and carboxylic acids reacting only in the presence of trace amounts of Lewis acid.

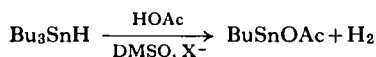
Finally, the reaction between trisubstituted silanes and silver perchlorate, yielding  $R_3SiClO_4$  esters, has been studied in a quantitative but not kinetic manner.  $AgH$  seems to be an intermediate. Variation in the  $R$  groups attached to silicon suggests that steric factors are important, implying nucleophilic participation even though in the hydrocarbon environment employed, the strongest nucleophile is the perchlorate anion (231).

Cleavage of  $sn-H$  bonds in both acidic and basic environments has been studied by Kuivila and Dessy and their co-workers. For  $Bu_3SnH$  in methanol the process involves general acid catalysis, with a Bronsted  $\alpha = 0.85$  (232a). Further studies appear to be necessary in order to distinguish between several possible transition states. Base-catalyzed reaction under these conditions seems to involve

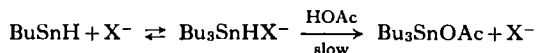


since the reaction is first order in substrate and lyate anion, and the reaction involves isotope effects for both substrate ( $sn-H/sn-D$ ) and lyate.

In DMSO (232b) the reaction



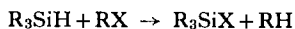
is third order, first order each in substrate, and acid, and first order and catalytic in  $X^-$ , the activity sequence being  $Cl^- > Br^- > I^-$ . The observed primary isotope effects ( $sn-H/snD$ ) indicate that the  $sn-H$  bond is being broken in the rate-determining step, and it is proposed that



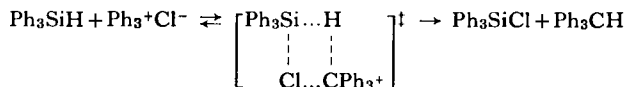
This is another example of nucleophilic catalysis, and emphasizes solvent characteristic, since in methanol, halide ion does not catalyze this process.

### E. Other Four-Center Processes

One rather clean reaction is

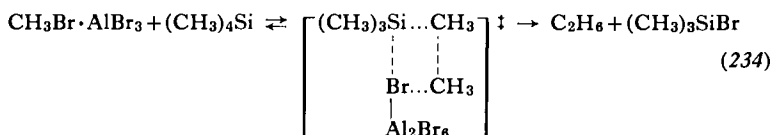


In the case of triphenylsilane and trityl chloride, this reaction is first order in both reactants in benzene (233). The reaction rate for modified substrates indicates that with respect to  $R_3CX$ , rate is a function of proclivity to ionize, trityl halides being more rapid than benzhydryl or allyl or *tert*-butyl halides. Indeed the latter required the presence of  $BBr_3$  as a catalyst. Within a given series,  $Cl > Br > I$ , phenylsilanes react more rapidly than alkyl silanes. A mechanism involving simultaneous nucleophilic attack of halide on silicon, and electrophilic attack on hydrogen by the carbonium ion is reasonable,

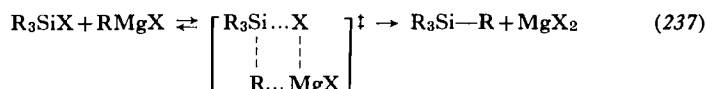
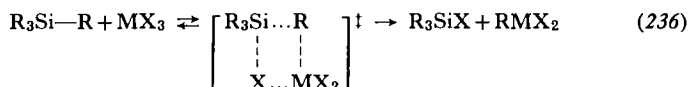
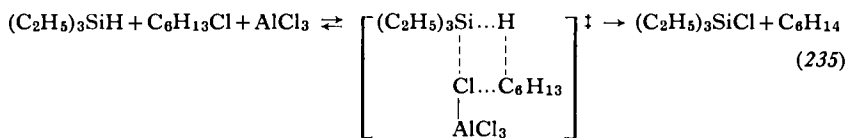


The reaction is also catalyzed by  $HCl$ , but remains first order in each of the reactants, suggesting formation of  $Ph_3C^+ HCl_2^-$ .

This reaction resembles the processes documented by Russell (234). He has reported that  $Me_4Si$  with  $MeBr$  and  $AlBr_3$  yields ethane, and compared his suggested transition state



with the following:



The first of the above has been postulated in an attempt to avoid high-energy intermediates, while the second is West's reaction *exactly*. The third has not

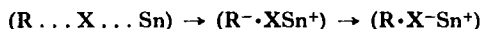
been proven, nor investigated, but the fourth has been substantiated by some work of Sommer and Reid.

Stereochemical support is derived from the fact (237b) that  $R_3Si^+Cl$  ( $R_3Si = \alpha$ -naphthylmethylphenylsilyl) reacts with organolithium reagents in the main to give inversion of configuration, but that  $R_3SiOMe$  reacts with  $EtMgBr$  with *retention* as does  $R_3SiH$  with  $BuLi$ . The former probably involves trigonal bipyramidal transition states, while the latter derive from quasicyclic transition states, as pictured above. The organogermanium hydride reacts with  $BuLi$  to give  $R_3Ge^*Li$  and thence with water or  $CO_2$  with retention (197).

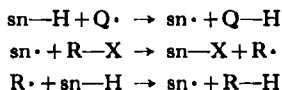
### F. *sn*—H/RX Reductions

In contrast, reduction of alkyl halides by the corresponding tin hydrides is radical in nature. Results leading to this view have been reviewed (238). Pertinent observations are: (a) Optically active  $\alpha$ -phenylethyl chloride gives racemic  $\alpha$ -deuteroethylbenzene. (b) Allylic and propargylic halides give both rearranged and unrearranged product, the latter yielding both propyne and allene. (c) Bromonortricyclene yields both nortricyclene and norbornene. (d) The relative reactivities of halides are in the proper form and order for radical chain processes. The latter data consist of two types of information. Pair competition experiments of halides indicated that the thermally induced reaction and that induced by azobisisobutyronitrile both yield the same relative reactivity ratios for the pairs, suggesting the same mechanistic pathway for both processes. Secondly, the reactivity sequence is not in the order for  $S_N2$  processes, but follows the order  $3^\circ > 2^\circ > 1^\circ$ . Nor is it in the  $S_N1$  order—*tert*- $BuX$  is faster than benzyl, and propargyl faster than allyl. Indeed the data parallel Szwarc's data on free radical abstraction of halide ion from alkyl halides by methyl radicals (239).

The halogen order is  $I > Br > Cl > F$ , and a polar factor seems to be involved, since electron-withdrawing substances facilitate reaction. This has been attributed to the polar contributions in the transition state



or to the effect of nonbonded repulsions between the lone electron in the *p* orbital of the attacking tin and the valence shell of the halogen.



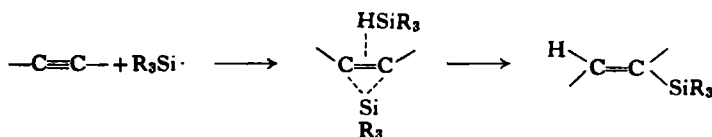


### G. si—H Additions

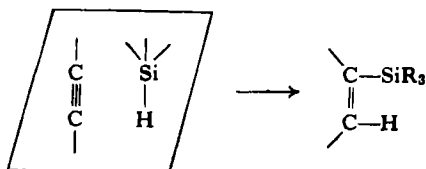
Addition reactions of si—H to olefins have been reviewed (215, 240). These involve mainly si—H substituted by —I groups. At the mechanistic level much is known, but little understood (241).

Thermal-peroxide-catalyzed, light-catalyzed, and supposed ionic mechanisms are available. The former involve silyl radical chain transfer, and because of the latter's ready formation (see Section A) little telomerization is encountered. In the majority of cases cited the addition to  $\text{CH}_2=\text{CHQ}$  gives  $\text{R}_3\text{SiCH}_2-\text{CH}_2\text{Q}$ , as might be expected on the basis of carbon radical stabilities. The supposed ionic reaction, catalyzed by metals such as platinum, and palladium (and the chloroplatinates and ruthenium chloride, via their reduction to metal) has been shown with vinyl acetate to give terminal —si, while addition to methylacrylate gives  $\text{CH}_3\text{SiCl}_2\text{CH}(\text{CH}_3)\text{COOCH}_3$ . Such additions are the basis for the supposed  $\text{si}^+ \dots \text{H}^-$  ionic pathway cited in the literature.

The reports that methyl methacrylate under similar conditions gives terminal —si, and the observation that a catalyst system made of  $\text{Bu}_3\text{N}$ , tetramethylene diamine, and  $\text{Cu(I)Cl}$  with acrylonitrile also gives terminal —si suggests that further controlled experiments are necessary. Benkeser has shown that the addition of  $\text{Cl}_3\text{SiH}$  to acetylenes catalyzed by metal is stereoselectively *cis*, while that involving peroxide catalysis is stereoselectively *trans*, even though in the later case terminal acetylenes give the more strained *cis* isomer. The literature suggests the following:

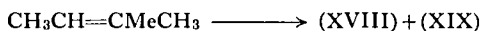
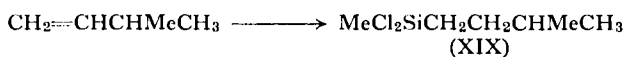
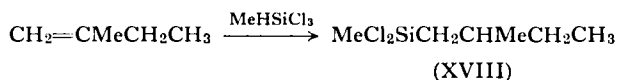


and

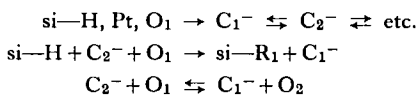


the latter being similar to the postulated mechanism for catalytic hydrogenation (presumably the metal, formed by reduction via si—H serves as a

surface for coordination.) The former is the analog of nonclassical intermediates in the addition of bromine to olefins. 1-Methylcyclohexene reacts with  $\text{Cl}_3\text{SiH}$  both by peroxide-induced and thermal-activated processes to give predominantly the *cis* isomer (*trans* addition) while chloroplatinic-acid-initiated addition to 1-methyl- $d_3$ -cyclohexene gives the *trans* isomer (*cis* addition) (241f). However, Saam and Speier (241e) have noted considerable recoverable rearranged olefin in these processes involving chloroplatinic acid initiation.

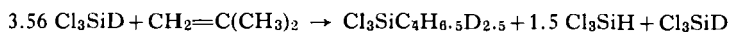


In the above cases pure olefin afforded the adducts shown, but recovered olefin proved to be a mixture of isomers. Excess silane suppressed the isomerizations. The fact that neither catalyst component itself isomerized olefins, but reaction mixtures at equilibrium could, suggested that the rearrangement catalyst was being formed during addition. Speier has favored a carbanionic mechanism,



the platinum-containing initiator forming a carbanion ( $\text{C}^-$ ) from olefin (O) and the  $\text{si-H}$  by hydride transfer. This is followed by carbanionic rearrangements (cf. organolithium reactions, Section II, A and D) primary carbanions being favored. The carbanions thus formed could attack  $\text{si-H}$ , perhaps via a quinquovalent silicon intermediate to give a potential hydride donor species, which would yield a chain ionic mechanism that is compatible with the low catalyst concentrations needed. Alternatively hydride transfer between olefin and carbanion could occur. Since the addition to 1-methyl- $d_3$ -cyclohexene gives *trans*-1-methyl-2-silylcyclohexane and cyclohexylmethylsilane with the entire deuterium content retained, it has been proposed that the carbanion rearrangement proceeds on a surface as a proton shift over a two-carbon distance by successive 1,2- or single 1,3-shifts intramolecularly, that surface release and reformation is necessary for further migration, and that hydride addition/elimination sequences are not

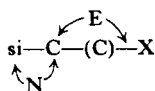
involved. Speier has questioned this, and shown that isobutylene reacts with  $\text{Cl}_3\text{SiD}$



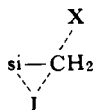
to give partially deuterated butylsilanes, showing definitively that the exchange occurred during the silane formation, not after. A large series of olefins clearly demonstrates that extensive deuterium incorporation at random positions occurs, in agreement with an addition-elimination sequence. Presumably in the methylcyclohexene case, the methylenecyclohexane required for the scrambling is a high-energy intermediate, and the intramolecular shift proposed is irreversible. Benkeser (241*h*) has recently reported data which cast further doubt on 1,3-shift mechanisms, and favors addition-elimination. Comparison with *b*-H and *sn*-H additions (242) should be made. Additions of *pb*-H have just been reported by Neumann.

### H. Neighboring Group Participation

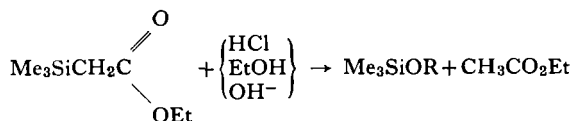
One class of reaction of organosilanes that deserves further mechanistic study involves alkylsilanes functionally substituted near the *c*-*si* bond. These systems can involve electrophilic and/or nucleophilic attack at the points indicated

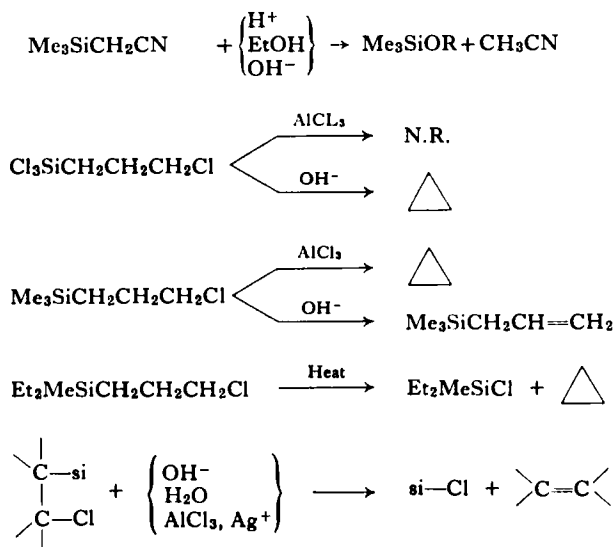


On the basis of kinetic data, simultaneous involvement of nucleophile with carbon and silicon has been postulated to account for the high reactivity of  $\alpha$ -chlorosilanes toward iodide ion (243, 244)

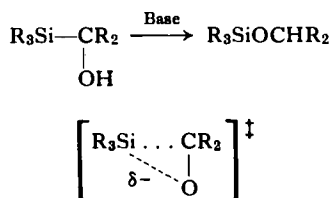


The reactions of  $\beta$ - and  $\gamma$ -substituted halo and oxy materials apparently may involve predominant electrophilic or nucleophilic catalysis, with solvolytic-type processes also being reported (245).



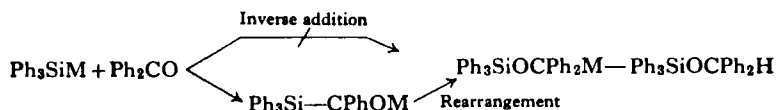


The similarities to the deoxymercuration processes reported earlier are obvious. Related is the rearrangement reported by Brook (246).

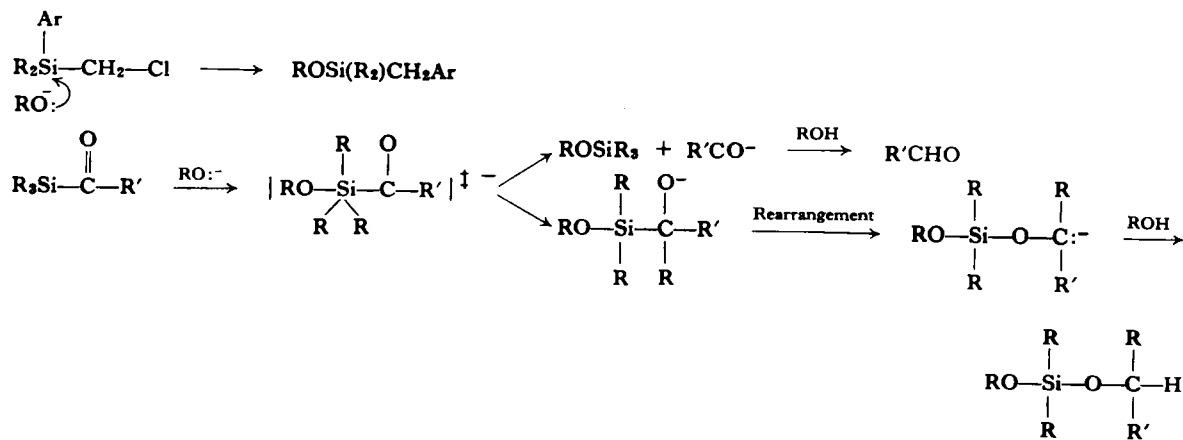


Details of the transition state are not clear, but retention of configuration at both centers (Si and C) is noted. Whether discharging of the incipient carbanion is beginning in the transition state, or the formed carbanion is asymmetrically solvated (cf. Cram and Streitweiser (47b)) so that discharge preserves its original configuration is unknown. The reaction is first order in silicone, and pseudo-first-order over-all.

It is felt that this rearrangement is involved in the addition of  $\text{R}_3\text{SiM}$  compounds to benzophenone (247),



Finally, there is the set of rearrangements (248, 249)

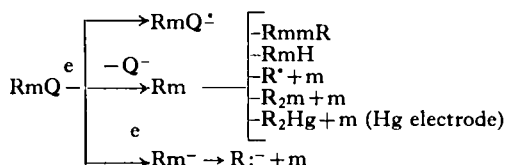


## VII

### CONCLUSION

The introduction referred to four areas in which strong parallels could be found between coordination chemistry, an offspring of inorganic chemistry, and organometallic chemistry, which saw its early growth in the hands of organic chemists. Three areas have been reviewed above. The fourth, because of the scope of this article, can be referred to only briefly.

Electrochemical reduction of organometallic assemblies,  $RmQ$ , where R is a  $\sigma$  or  $\pi$ -complexed organic moiety, Q is oxy-function, halide or R, and m is a metal, indicate nine possible fates for the assembly



All of these find obvious parallels in the chemistry of coordination compounds (250).

We can see that in the area of organometallic reaction mechanisms there is considerable room for well-conceived mechanistic studies, particularly in those cases where the reagents are extremely difficult to handle, and where absolute reaction rate constants are exceedingly high. The nature of the carbon-metal bond in various solvents, and the aggregation of the organometallic reagent in many cases also needs re-examination. The chemistry of subvalent materials also needs attention, and as the work outlined in this chapter indicates, in all of this the vocabulary and philosophy of the coordination chemist will be extremely valuable. Such studies, combining, as they must, the areas of physical, inorganic and organic chemistry with the tools of the analytical chemist illustrate the value and need of destroying conventional barriers that exist in chemistry.

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# Metal $\pi$ -Complexes Formed by Seven-Membered and Eight-Membered Carbocyclic Compounds

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## I

## INTRODUCTION

In 1959 Brown (18) concluded on theoretical grounds that the most stable complexes of transition metals with planar, carbocyclic systems  $C_nH_n$  would occur with values of  $n$  of 5 and 6, and that stability would fall off with increasing ring size. Thus at first the prospects of obtaining complexes of the ferrocene type with seven- and eight-membered rings did not appear promising. Nevertheless characterization of many types of  $\pi$  complex including monoolefin, conjugated, and unconjugated diolefin (10, 64, 65, 77),  $\pi$ -allyl (75), and  $\pi$ -cyclopentadienyl and  $\pi$ -arene complexes (51, 66,

135) prompted the isolation of many complexes of seven- and eight-membered rings. In this review we shall consider the complexes of the following species:

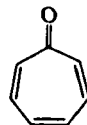
### *Seven-Membered Rings*



Tropylium ion



Cycloheptatriene



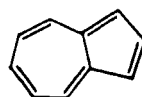
Cycloheptatrienone



Cyclohepta-1,3-diene



Cycloheptene



Azulene

### *Eight-Membered Rings*



Cyclooctatetraene



Cycloocta-1,3,5-triene



Cycloocta-1,3,6-triene



Cycloocta-1,5-diene



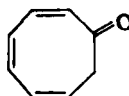
Cycloocta-1,4-diene



Cycloocta-1,3-diene



Cyclooctene



Cyclooctatrienone

## II

### COMPLEXES WITH SEVEN-MEMBERED RINGS AS LIGANDS

The tropylium ion,  $C_7H_7^+$ , is an aromatic six- $\pi$  electron system (44) which would be expected to form  $\pi$  complexes with transition metals analogous to

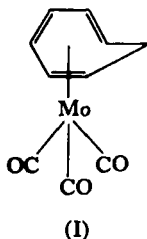
those formed by  $C_5H_5^-$  and  $C_6H_6$ . All attempts to prepare such complexes starting from tropylium bromide have been unsuccessful; for example, sodiopentacarbonyl manganate(-1) and tropylium bromide react to give ditropyl (1). The latter is probably formed by decomposition of an unstable  $\sigma$ -tropyl complex,  $C_7H_7Mn(CO)_5$ .



All successful syntheses of tropylium  $\pi$  complexes start from cycloheptatriene.

### A. Cycloheptatriene and Tropylium Metal Carbonyls

Cycloheptatriene and a number of its alkyl derivatives react with the Group VI metal carbonyls giving orange-red crystalline, diamagnetic complexes of general formula (cycloheptatriene) $M(CO)_3$  ( $M = Cr, Mo, \text{ or } W$ ) (1, 2, 11). Infrared and NMR studies show the presence of coordinated cycloheptatriene in these complexes (1, 11, 96), and this is confirmed by X-ray study of (cycloheptatriene) $Mo(CO)_3$  (45a), which shows the six olefinic CH groups of the ring to be nearly coplanar, with the methylene  $CH_2$  group bent away from this plane away from the metal atom (I). The C—C bond lengths of the ring are approximately those expected for a

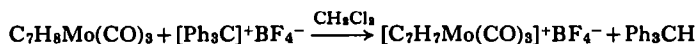


cyclic polyolefin, and there is no equalization as observed in (butadiene) $Fe(CO)_3$  and related structures [see Pettit (118) and references cited therein]. It may be noted that the six olefinic CH groups of free cycloheptatriene are not coplanar, the molecule having a boat configuration, as shown by electron diffraction (128). An X-ray study of thujic acid [7,7-dimethylcycloheptatriene-3-carboxylic acid] shows a similar configuration (38).

In the Group VI complexes, cycloheptatriene behaves formally as a six  $\pi$ -electron donor, with each double bond supplying two electrons to the metal so that, with six electrons from the CO's, the metal attains the rare

gas configuration. It has been suggested that cycloheptatriene is a poorer donor than benzene, since the dipole moment of (cycloheptatriene)Cr(CO)<sub>3</sub> (4.52 D) is less than that of (benzene)Cr(CO)<sub>3</sub> (5.08 D) (119). The complex (cycloheptatriene)Mo(CO)<sub>3</sub> reacts with a variety of ligands (L) with displacement of the ring, giving *cis*-trisubstitution products of general formula Mo(CO)<sub>3</sub>L<sub>3</sub> (3, 33a).

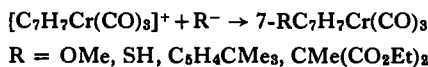
Dauben and Honnen (36) first showed that triphenylmethyl fluoroborate abstracts hydride ion from (cycloheptatriene)Mo(CO)<sub>3</sub> to give  $\pi$ -tropylium-molybdenum tricarbonyl fluoroborate



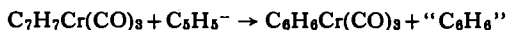
The orange, air-stable salt shows two C—O stretching frequencies in its infrared spectrum, and only one proton resonance line in D<sub>2</sub>SO<sub>4</sub>, in accord with the presence of a C<sub>7</sub>H<sub>7</sub> ring symmetrically bound to the metal. The chromium and tungsten analogs have also been prepared (37, 110). All three tropylium complexes are more stable with respect to hydrolysis (C<sub>7</sub>H<sub>7</sub><sup>+</sup> + H<sub>2</sub>O → C<sub>7</sub>H<sub>7</sub>OH + H<sup>+</sup>) than is tropylium fluoroborate itself (101).

The hydride ion abstraction reaction can be reversed by adding sodium borohydride to the  $\pi$ -tropylium complexes (109, 110), e.g., [C<sub>7</sub>H<sub>7</sub>Cr(CO)<sub>3</sub>]<sup>+</sup> + H<sup>−</sup> → C<sub>7</sub>H<sub>8</sub>Cr(CO)<sub>3</sub>. Other anions react with the  $\pi$ -tropylium-chromium carbonyl cation in three different ways:

(1) Normal reaction, forming 7-substituted cycloheptatriene complexes (110).

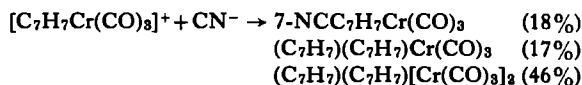


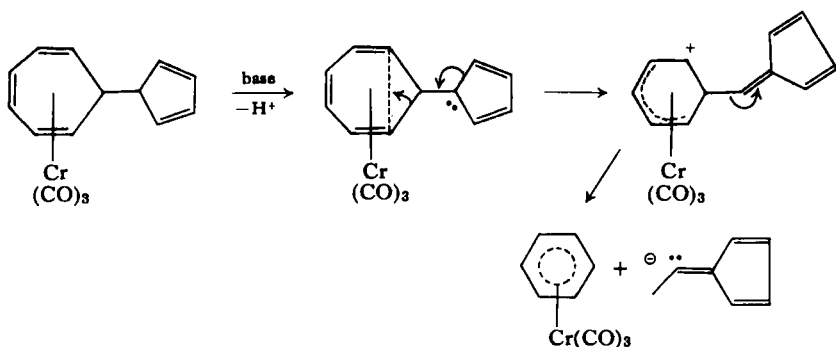
(2) Rearrangement reaction forming benzenechromium tricarbonyl, e.g., with excess cyclopentadienide anion (111).



The benzene ring in the C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> is known to be derived entirely from the original seven-membered ring, and, provided excess C<sub>5</sub>H<sub>5</sub><sup>−</sup> is not used, 7-(C<sub>5</sub>H<sub>5</sub>)(C<sub>7</sub>H<sub>7</sub>)Cr(CO)<sub>3</sub> can be isolated from the reaction. A possible mechanism for this remarkable reaction is shown on p. 357.

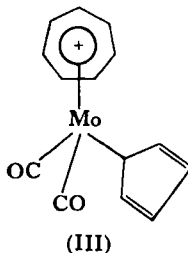
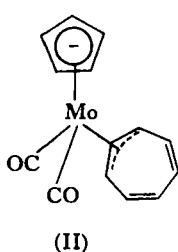
(3) Abnormal reaction, forming mono- and bis(tricarbonyl) complexes of ditropyli, e.g.,





Similar abnormal reactions occur with anions such as  $\text{HCO}_3^-$ ,  $\text{MeCO}_2^-$ ,  $\text{NH}_2^-$ ,  $\text{C}_6\text{H}_5^-$ , and  $\text{PhCONH}^-$ , and with zinc dust (112). The mechanism of this coupling reaction is obscure, but  $\text{C}_7\text{H}_7\text{Cr}(\text{CO})_3$  radical intermediates may well be involved.

Complexes of the type  $\pi\text{-C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ , or  $\text{I}$ ) have been prepared, by treating  $\pi\text{-C}_7\text{H}_7\text{Mo}(\text{CO})_3$  cation with the appropriate halide ion (14).<sup>1</sup> The iodo complex reacts with  $\text{NaMn}(\text{CO})_5$  to give a dark green complex  $\pi\text{-C}_7\text{H}_7\text{Mo}(\text{CO})_2\text{Mn}(\text{CO})_5$ , containing a mixed metal-metal bond, and with  $\text{NaC}_5\text{H}_5$  to give an orange diamagnetic complex  $\text{C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{-C}_7\text{H}_7$  (91, 92). In this complex, the  $\text{C}_7\text{H}_7$  group must be functioning as a three- $\pi$ -electron donor, i.e., as a substituted  $\pi$ -allyl group, in order that molybdenum achieves the rare gas configuration (II).



However, the complex shows only two signals in its proton NMR spectrum at 4.93  $\tau$  and 5.21  $\tau$  in a 5:7 intensity ratio, and the free double bonds of the  $\text{C}_7\text{H}_7$  group fail to react with hydrogen or with  $\text{Fe}(\text{CO})_5$ . An adduct is formed with tetracyanoethylene, but it could not be obtained pure. The spectrum of the complex  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_7\text{H}_7$  is therefore analogous to that of  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$  (see Section III, B), and a similar rapid rotation of the

<sup>1</sup> See R. B. King, "Transition Metal Compounds." Academic Press, New York, 1965.

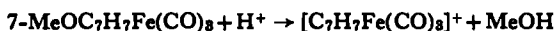
metal-to-ring bond about the carbocyclic ring must be assumed. The alternative structure  $\pi\text{-C}_7\text{H}_7\text{Mo(CO)}_2 \sigma\text{-C}_5\text{H}_5$  (III) was ruled out as being incompatible with the observed NMR spectrum, and on the grounds of the failure to isolate alkyls and aryls of the type  $\pi\text{-C}_7\text{H}_7\text{Mo(CO)}_2\text{R}$  (R = Me, Ph, etc.) from  $\pi\text{-C}_7\text{H}_7\text{Mo(CO)}_2\text{I}$ . The orange color of the complex, in contrast to the green or blue color of most uncharged  $\pi$ -tropylium complexes, also suggests the  $\pi$ -allyl structure to be correct.<sup>1a</sup>

Cycloheptatriene reacts with vanadium hexacarbonyl to afford in 21% yield a dark green, diamagnetic  $\pi$ -tropylium-vanadium tricarbonyl [ $\pi\text{-C}_7\text{H}_7\text{V(CO)}_3$ ] which is isoelectronic with [ $\pi\text{-C}_7\text{H}_7\text{Cr(CO)}_3$ ]<sup>+</sup> (132).<sup>2</sup> Infrared and NMR spectra suggest, and an X-ray study (6) confirms, the presence of the tropylium cation symmetrically bound to the metal. The stability order (indicated qualitatively by sensitivity to air in solid state and in solution) in the isoelectronic series of aromatic metal tricarbonyls is



This is as expected, since it is the order of increasing positive charge on the metal. The NMR spectrum of  $\pi\text{-C}_7\text{H}_7\text{V(CO)}_3$  is more complex than that of other  $\pi$ -tropylium complexes (71, 132). At  $-50^\circ\text{C}$  there is one sharp signal corresponding to the seven equivalent protons of the ring, as expected, but at room temperature and above, the signal consists of two broad maxima separated by about 10 cps. Fritz and Kreiter (71) reject the possibility of spin-spin coupling with  $\text{V}^{51}$ , and suggest that, in solution at room temperature, the seven-membered ring of the complex is distorted by localization of its positive charge on one carbon atom.

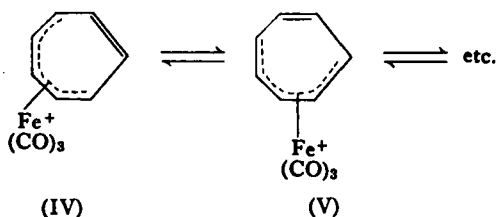
Cycloheptatriene does not react with  $\text{Fe(CO)}_5$  to give the expected dicarbonyl complex  $\pi\text{-C}_7\text{H}_8\text{Fe(CO)}_2$ , but forms instead a mixture of tricarbonyl complexes derived from cycloheptatriene and cyclohepta-1,3-diene (20, 35). This work, together with protonation and related reactions of the free double bond of  $\pi\text{-C}_7\text{H}_8\text{Fe(CO)}_3$ , have been summarized by Pettit and Emerson (118). More recently, Pettit and co-workers (101) have shown that (7-methoxycycloheptatriene) $\text{Fe(CO)}_3$  is protonated by fluoroboric acid with loss of methanol to give the  $\pi$ -tropylium-iron tricarbonyl cation.



<sup>1a</sup> Note added in proof: The  $\pi\text{-C}_7\text{H}_7$  resonance in the NMR spectrum of  $\pi\text{-C}_5\text{H}_5\text{Mo(CO)}_3$   $\pi\text{-C}_7\text{H}_7$  is broadened on cooling to  $-40^\circ$ , while the  $\pi\text{-C}_5\text{H}_5$  resonance remains unchanged (93b).

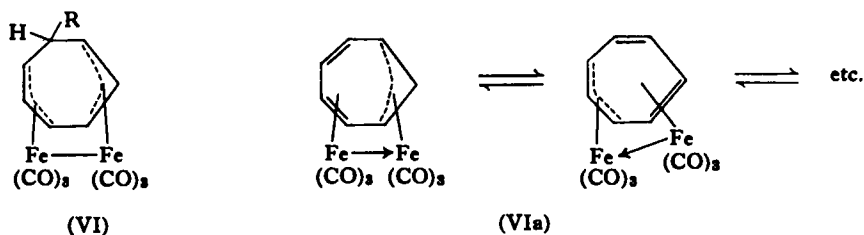
<sup>2</sup> An ionic [ $\pi\text{-C}_7\text{H}_7\text{V}-\pi\text{-C}_7\text{H}_8$ ] $[\text{V(CO)}_6]$  is also produced (see Section II, B).

The infrared spectrum of the fluoroborate salt indicates the presence of an unsymmetrical seven-membered ring with an uncomplexed *cis* double bond, but the NMR spectrum shows only one proton resonance signal, and it must be assumed that the  $\text{Fe}(\text{CO})_3$  group is rotating rapidly about the seven-membered ring, as in  $\pi\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2\text{C}_7\text{H}_7$  and  $\pi\text{-C}_8\text{H}_8\text{Fe}(\text{CO})_3$  (see Section III, B). This has been termed valence tautomerism between equivalent structures such as (IV) and (V) in solution.



It may be noted that  $[\text{C}_7\text{H}_7\text{Fe}(\text{CO})_3]^+$  cannot be obtained by hydride ion abstraction from  $\text{C}_7\text{H}_8\text{Fe}(\text{CO})_3$  with triphenylmethyl fluoroborate, because the triphenylmethyl cation adds to the free double bond (35).

Orange-red, crystalline, binuclear complexes of general formula (triene)- $\text{Fe}_2(\text{CO})_6$  are obtained from the reaction of  $\text{Fe}_2(\text{CO})_9$  with cycloheptatriene or its 7-methoxy derivative (46). The equivalence of the iron atoms in the Mössbauer spectrum of  $\pi\text{-C}_7\text{H}_8\text{Fe}_2(\text{CO})_6$ , its high dipole moment (4.8 D), and its NMR spectrum accord with a bis( $\pi$ -allyl) structure containing an iron-iron bond (VI). On protonation with  $\text{HBF}_4$ , both the cycloheptatriene and 7-methoxycycloheptatriene complexes give a cation  $[\text{C}_7\text{H}_7\text{Fe}_2(\text{CO})_6]^+$ , which shows only one proton resonance signal at  $5.2\tau$  in liquid  $\text{SO}_2$ , presumably owing to valence tautomerism between equivalent structures and rapid rotation of the metal-metal bond about the seven-membered ring (VIa).



Cycloheptatriene and cobalt carbonyl react on irradiation to give  $\pi\text{-C}_7\text{H}_7\text{Co}(\text{CO})_3$  as a dark red, air-sensitive liquid (92). This can be regarded



as a substituted  $\pi$ -allyl cobalt tricarbonyl, with the  $C_7H_7$  radical functioning as a three- $\pi$ -electron donor as in  $\pi-C_5H_5Mo(CO)_2C_7H_7$ . Again, however, there is only one proton resonance signal at 4.49  $\tau$  in carbon disulfide due to the  $C_7H_7$  protons, and the free double bonds are relatively unreactive to addition, so that valence tautomerism must again be invoked.

### B. Other Cycloheptatriene and Tropylium-Metal Complexes

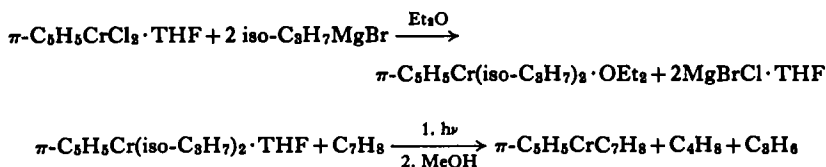
Although no bis( $\pi$ -tropylium)-metal complexes analogous to  $Fe(C_5H_5)_2$  and  $Cr(C_6H_6)_2$  have been isolated, a number of complexes containing seven-membered rings analogous to the mixed complexes, such as  $C_5H_5MC_6H_6$  ( $M = Cr, Mn$ ), have been obtained. The complex  $\pi-C_5H_5V(CO)_4$  reacts with cycloheptatriene to give purple, paramagnetic crystals of  $\pi-C_5H_5V-\pi-C_7H_7$  [ $\mu_{eff} = 1.69$  B.M.], isoelectronic with  $V(C_6H_6)_2$  (95), being the first neutral  $C_7H_7$ -metal complex to be isolated. The simplicity of the infrared spectrum in the 1400–1000  $cm^{-1}$  region caused some scepticism (72) about its initial formulation as a  $\pi$ -tropylium complex, but a recent X-ray study (47) showed that the proposed structure (95) was correct. A surprising feature of the structure is that the vanadium atom is markedly nearer to the seven-membered ring than to the five-membered ring ( $V-C_7H_7$  distance, 1.50 Å;  $V-C_5H_5$  distance = 1.90 Å), presumably because this allows better overlap with the  $\pi$ -orbitals of the larger ring. It has also been suggested that there is resonance between  $C_7H_7^+V^0C_5H_5^-$  and  $C_7H_7^-V^{2+}C_5H_5^-$  (95).

Another species isoelectronic with  $V(C_6H_6)_2$  is the ( $\pi$ -tropylium)-(cycloheptatriene)vanadium cation,  $[\pi-C_7H_7VC_7H_8]^+$ , which is formed as its  $[V(CO)_6]^-$  salt from the reaction of vanadium carbonyl with cycloheptatriene (21). The complex  $\pi-C_7H_7V(CO)_3$ , referred to in the preceding Section, is formed simultaneously. The salt is an insoluble, red-brown solid with  $\mu_{eff} = 1.78$  B.M., and a C—O stretching frequency at 1850  $cm^{-1}$  characteristic of  $[V(CO)_6]^-$ . The tetraphenylborate salt can be prepared by anion exchange. A likely precursor of  $\pi-C_7H_7V(CO)_3$  and  $[\pi-C_7H_7VC_7H_8][V(CO)_6]$  in the above reaction is (cycloheptatriene) $V(CO)_3$  (21). The hydrogen lost when this decomposes is not evolved, but is probably transferred to the cycloheptatriene.

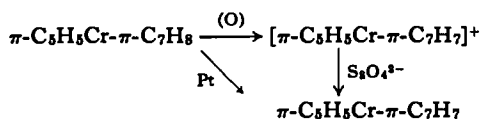
Attempts to prepare  $\pi-C_5H_5Cr-\pi-C_7H_7$  from  $[\pi-C_5H_5Cr(CO)_3]_2$  and cycloheptatriene have been unsuccessful (92). It is necessary to start from  $\pi$ -cyclopentadienyl chromium compounds which contain ligands more easily replaced than carbon monoxide. For example, the benzene ring of

$\pi$ -C<sub>5</sub>H<sub>5</sub>Cr- $\pi$ -C<sub>6</sub>H<sub>6</sub> is replaced by cycloheptatriene in the presence of anhydrous aluminum chloride to give yellow-green [C<sub>5</sub>H<sub>5</sub>Cr C<sub>7</sub>H<sub>7</sub>]<sup>+</sup> cation, which is isolated as PF<sub>6</sub><sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, or Reineckate salts (48). The magnetic moment of [C<sub>5</sub>H<sub>5</sub>Cr C<sub>7</sub>H<sub>7</sub>]<sup>+</sup> is 2.0 B.M., indicating one unpaired electron. This is as expected, since the cation is isoelectronic with [Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>]<sup>+</sup> and with C<sub>5</sub>H<sub>5</sub>VC<sub>7</sub>H<sub>7</sub>. Reduction with alkaline Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> gives the uncharged diamagnetic, air-sensitive and green compound, C<sub>5</sub>H<sub>5</sub>CrC<sub>7</sub>H<sub>7</sub>, isoelectronic with Cr(C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>. The NMR spectrum shows the expected two signals in a 5:7 intensity ratio, there being no evidence for a localized carbonium ion structure as suggested for C<sub>7</sub>H<sub>7</sub>V(CO)<sub>3</sub>. The finite dipole moment of C<sub>5</sub>H<sub>5</sub>CrC<sub>7</sub>H<sub>7</sub> ( $\mu$  = 0.73 D in cyclohexane) has been interpreted as indicating a small contribution from an ionic structure C<sub>5</sub>H<sub>5</sub><sup>-</sup>CrC<sub>7</sub>H<sub>7</sub><sup>+</sup> (48).

( $\pi$ -Cyclopentadienyl)(cycloheptatriene)chromium, a probable intermediate in the above reaction, has been obtained in 70% yield by displacing alkyl groups, especially isopropyl groups, on chromium(III) in the presence of cycloheptatriene (55).

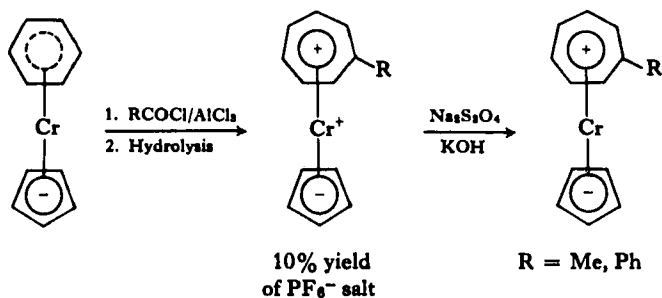


The brown, air-sensitive complex has one unpaired electron ( $\mu_{\text{eff}}$  = 1.63 B.M.), and a dipole moment of 1.1 D. Slow oxidation in aqueous acetone affords C<sub>5</sub>H<sub>5</sub>CrC<sub>7</sub>H<sub>7</sub>, and dehydrogenation gives C<sub>5</sub>H<sub>5</sub>CrC<sub>7</sub>H<sub>7</sub> directly. These relationships are summarized in the scheme

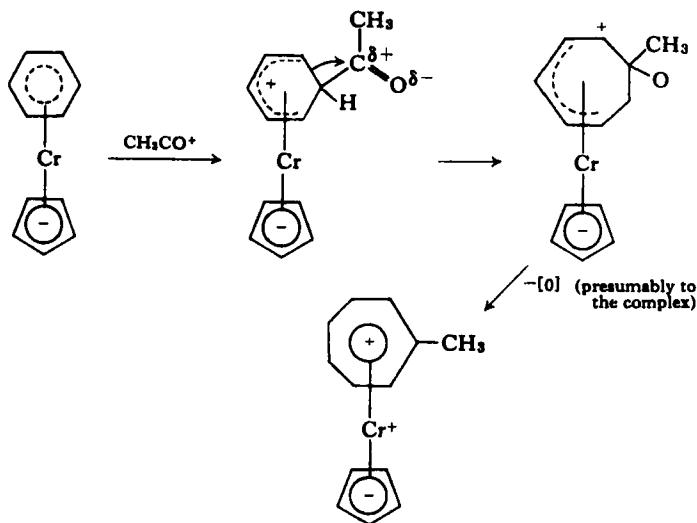


The complex  $\pi$ -C<sub>5</sub>H<sub>5</sub>Cr- $\pi$ -C<sub>7</sub>H<sub>7</sub> can also be obtained (2% yield) by treating anhydrous chromium chloride and a mixture of cyclopentadiene and cycloheptatriene with isopropyl Grignard reagent (92). Use of VCl<sub>3</sub> in place of CrCl<sub>3</sub> is reported to give less than 0.1% yield of  $\pi$ -C<sub>5</sub>H<sub>5</sub>V- $\pi$ -C<sub>7</sub>H<sub>7</sub>.

Derivatives of C<sub>5</sub>H<sub>5</sub>CrC<sub>7</sub>H<sub>7</sub> containing substituted tropylium cations appear as by-products in the Friedel-Crafts acylation of the benzene ring of C<sub>5</sub>H<sub>5</sub>CrC<sub>6</sub>H<sub>6</sub> (49).



This remarkable ring-expansion reaction is the only route so far known to a seven-membered ring complex which does not start from a seven-membered ring hydrocarbon. The reaction may well be related mechanistically to the ring collapse of  $[\text{C}_7\text{H}_7\text{Cr}(\text{CO})_3]^+$  (Section II, A), with metal-stabilized, localized carbonium ion intermediates, e.g.,

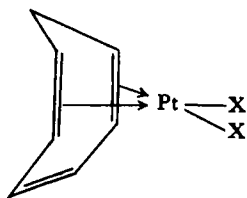


The corresponding manganese(I) complexes ( $\pi\text{-C}_5\text{H}_5\text{Mn-}\pi\text{-C}_7\text{H}_7\text{R}$ ) ( $\text{R} = \text{Me, Ph}$ ) can also be obtained by acylation of  $\pi\text{-C}_5\text{H}_5\text{Mn-}\pi\text{-C}_6\text{H}_6$ , but they cannot be reduced to uncharged  $\text{Mn}(0)$  species (49).

The only other  $\pi$ -tropylium complexes reported are compounds of formula  $[\text{C}_7\text{H}_7\text{PtBr}_2]_2$  and  $\text{C}_7\text{H}_7\text{PtBr}_3$  obtained by treating platinum(IV) bromo compounds with cycloheptatriene (50). The complex  $[\text{C}_7\text{H}_7\text{PtBr}_2]_2$  has recently been shown to be a mixture of  $(\text{C}_7\text{H}_7)_2\text{PtBr}_6$  and (cycloheptatriene) $\text{PtBr}_2$  (98); (cycloheptatriene) $\text{PtCl}_2$  can also be obtained by displacing

ethylene from  $[C_2H_4PtCl_2]_2$  with cycloheptatriene (5). In these platinum(II) complexes, cycloheptatriene is behaving as a chelate diolefin similar to cycloocta-1,5-diene (see Section III, A, 1), and its configuration is probably "boat," as in the free olefin (VII).

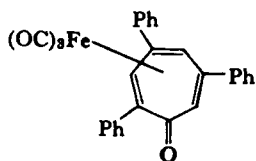
In contrast to the behavior with platinum, a number of rhodium(I) and iridium(III) complexes react with cycloheptatriene to form complexes of the isomeric bicyclic chelate diolefin, norbornadiene (15, 137).



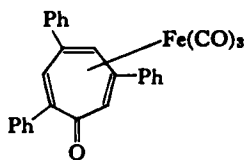
(VII)

### C. Complexes of Cycloheptatrienone (Tropone)

The seven-membered cyclic ketone, tropone,  $C_7H_7O$ , might be expected to form complexes like those of cycloheptatriene. Only the iron carbonyl complexes have been studied in any detail. Troponeiron tricarbonyl is one of the products of the reaction between acetylene and  $Fe_2(CO)_9$  (131a); this reaction, and the properties of the complex, have been summarized by Pettit and Emerson (118). Reaction between  $Fe_3(CO)_{12}$  and phenylacetylene gives two isomeric complexes of formula (2,4,6-triphenyltropone) $Fe(CO)_3$ , which are assigned structures (VIII) and (IX) (16).



(VIII)



(IX)

X-ray studies of (tropone) $Fe(CO)_3$  (43) and of one of the (2,4,6-triphenyltropone) $Fe(CO)_3$  isomers (126) confirm that one of the double bonds is not attached to the metal. Attempts to prepare complexes such as (tropone)- $M(CO)_3$  ( $M = Cr, Mo$ ) have not been successful (90).

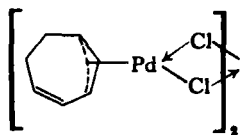
### D. Complexes of Cyclohepta-1,3-diene

Relatively little work has been done on complexes of cyclohepta-1,3-diene, and almost none on complexes of the 1,4-isomer. The iron tricarbonyl complex  $1,3\text{-C}_7\text{H}_{10}\text{Fe}(\text{CO})_3$  is obtained from  $\text{Fe}(\text{CO})_5$  and the diene, and also from  $\text{Fe}(\text{CO})_5$  and cycloheptatriene (19, 35). More recently, a complex of zero-valent iron containing only cyclohepta-1,3-diene and cycloheptatriene, has been obtained by a reductive Grignard reaction on ferric chloride (57).

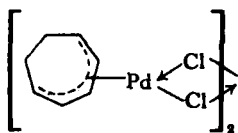


The yellow-orange complex is very air-sensitive and is thermally unstable, but its existence as an isolable species indicates that olefin complexes of low-valent metals may be stable even when groups such as CO are absent. A yellow, more stable ruthenium(0) analog has been mentioned briefly (57).

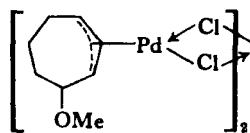
The reaction of cyclohepta-1,3-diene with palladium(II) compounds has been investigated in some detail. As expected for this element,  $\pi$ -allyl complexes are the main products (75). Palladium(II) carbonyl chloride  $[\text{Pd}(\text{CO})\text{Cl}_2]_2$  and cyclohepta-1,3-diene were first reported to form a yellow complex  $(\text{C}_7\text{H}_{10}\text{PdCl})_2$  (62), later amended to  $(\text{C}_7\text{H}_{11}\text{PdCl})_2$ , i.e., a  $\pi$ -cycloheptenyl derivative analogous to the corresponding derivative  $(\text{C}_6\text{H}_9\text{PdCl})_2$  from cyclohexa-1,3-diene (63). The same complex has since been obtained by reaction of cyclohepta-1,3-diene with  $\text{PdCl}_2$  in glacial acetic acid (82), and by heating methanolic  $\text{Na}_2\text{PdCl}_4$  with the diene (122); both groups of workers reformulate the complex as a cyclohepta-2,4-dienyl derivative  $(\text{C}_7\text{H}_9\text{PdCl})_2$ . Hüttel and co-workers (82) consider structure (X)



(X)



(XI)



(XII)

to be most reasonable on the basis of infrared and NMR spectra. The band at  $1625\text{ cm}^{-1}$ , which is presumably the  $\text{C}=\text{C}$  stretching frequency of the uncomplexed double bond, is very weak and broad, and, on this basis, Robinson and Shaw (122) prefer the alternative structure (XI), in which the cycloheptadienyl group donates five  $\pi$  electrons to palladium, leading to an 18-electron rather than the usual 16-electron configuration for the metal.

There is some evidence from the UV spectrum for conjugation of the "free" double bond with the  $\pi$ -allyl group of structure (X) (82). A 4-methoxycyclohept-2-enyl complex (XII) has also been isolated from the reaction of cyclohepta-1,3-diene with methanolic  $\text{Na}_2\text{PdCl}_4$  at room temperature (122). The halogen bridges in all these complexes can be split by pyridine, thallos acetylacetonate, and sodium cyclopentadienide to give mononuclear complexes of the type  $\text{Pd}(\pi\text{-allyl})\text{LCl}$  ( $\text{L} = \text{py}$ ,  $\text{acac}$ ,  $\text{C}_5\text{H}_5$ ).

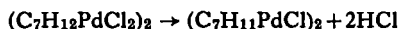
### E. Complexes of Cycloheptene

Cycloheptene can be extracted by aqueous silver nitrate, and although no stable complex has been isolated, the equilibrium constant for the reaction

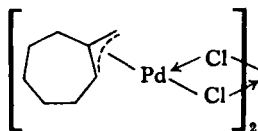


has been determined by distribution methods (129, 130). The order of formation constants of a series of silver-cyclic olefin complexes is cyclopentene > cycloheptene > cyclohexene > *cis*-cyclooctene. Relief of ring strain and, in the larger rings, interannular interference of hydrogen atoms, are probably important factors which determine the stability order.

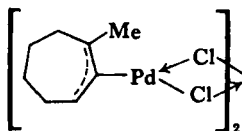
Cycloheptene reacts with  $\text{PdCl}_2$  in acetic acid at room temperature giving a brown, insoluble olefin complex  $\text{C}_7\text{H}_{12}\text{PdCl}_2$ , which is probably dimeric with bridging chlorine atoms (82). It is much more stable thermally than the corresponding ethylene complex, and in agreement with the data on silver-olefin complexes, it is more stable than the corresponding cyclohexene complex also. On heating in glacial acetic acid, hydrogen chloride is eliminated with formation of a  $\pi$ -cycloheptenyl complex (82).



1-Methylcycloheptene reacts similarly with  $\text{PdCl}_2$ , though the initially formed olefin complex is much less stable in this case and cannot be obtained pure. It readily eliminates hydrogen chloride to form a  $\pi$ -allyl complex with the *exo* configuration (XIII) rather than the *endo* configuration (XIV) as shown by its NMR spectrum (82). In the *exo* configuration, planarity of the  $\pi$ -allyl group is more readily achieved.



(XIII)

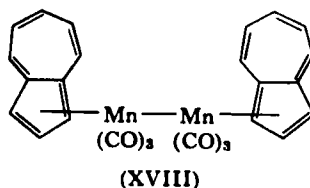
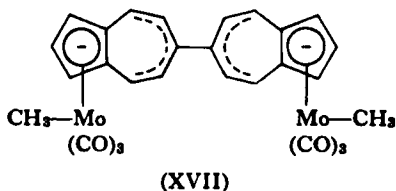
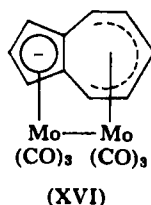
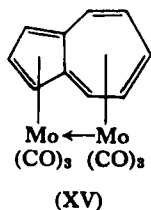


(XIV)

Cycloheptene is reported to displace one CO group from  $\pi\text{-C}_5\text{H}_5\text{Mn(CO)}_3$  on heating and irradiation, giving a yellow, sublimable, air-stable complex  $\pi\text{-C}_5\text{H}_5\text{Mn(CO)}_2\text{C}_7\text{H}_{12}$ , in which the  $\text{C}=\text{C}$  stretching frequency of the olefin is shifted from  $1655\text{ cm}^{-1}$  to  $1484\text{ cm}^{-1}$  (53). The corresponding cyclohexene complex could not be isolated, in agreement with considerations of ring strain in the olefins. No other metal carbonyl complexes of cycloheptene have been reported.

### F. Complexes of Azulene

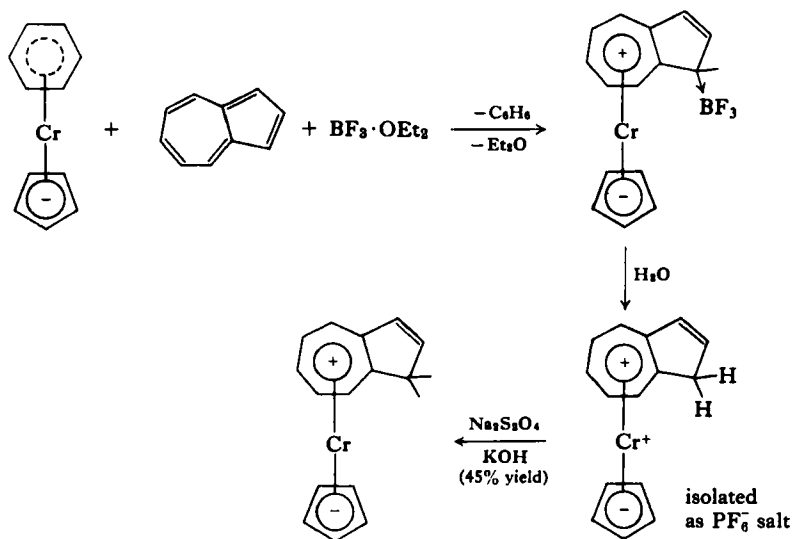
Azulene complexes are of particular interest, owing to the possibilities of bonding either from the seven-membered ring, or from the five-membered ring, or from both. Azulene and several of its alkyl derivatives react with  $\text{Fe(CO)}_5$  to give complexes of the type  $(\text{azulene})\text{Fe}_2(\text{CO})_5$  (19), whose properties and suggested structures have been reviewed elsewhere (10, 118). A polynuclear complex  $(\text{azulene})_2\text{Fe}_3(\text{CO})_{13}$  has also been reported (19). With  $\text{Mo(CO)}_6$ , dark red, sparingly soluble complexes of general formula  $(\text{azulene})\text{Mo}_2(\text{CO})_6$  are formed (19) for which structures (XV) and (XVI) have been suggested (93), to account for the observed diamagnetism.



On treatment with sodium amalgam, followed by methyl iodide,  $(\text{azulene})\text{-Mo}_2(\text{CO})_6$  gives a complex of the unexpected formula  $[\text{CH}_3\text{Mo(CO)}_3\text{azulene}]_2$ , which apparently contains one azulene ring per metal atom (93). Presumably, sodium breaks the bond between metal and seven-membered ring, giving a binuclear, substituted  $(\text{CH}_3)(\pi\text{-cyclopentadienyl})\text{Mo(CO)}_3$

compound (XVII). In the complex  $(\text{azulene})_2\text{Mn}_2(\text{CO})_6$  formed from  $\text{Mn}_2(\text{CO})_{10}$  and azulene, the seven-membered ring is apparently not coordinated to the metal (XVIII) (19).

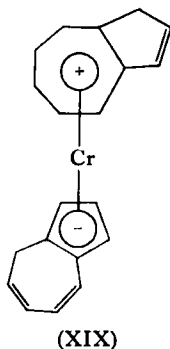
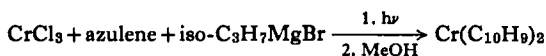
Fischer and Breitschaft (49a) have prepared complexes which contain the azulonium cation,  $\text{C}_{10}\text{H}_9^+$ , by displacement of benzene from  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_6\text{H}_6$  as shown in the scheme



The  $[\pi\text{-C}_5\text{H}_5\text{CrC}_{10}\text{H}_9]^+$  cation may be regarded as a derivative of  $[\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_7\text{H}_7]^+$ , and is likewise yellow and paramagnetic ( $\mu_{\text{eff}} = 2.04$  B.M.). It can also be reduced to the dark green, air-sensitive, diamagnetic complex  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_{10}\text{H}_9$ , though this process cannot be reversed by air oxidation (cf.,  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_7\text{H}_7$ ). The free double bond of  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_{10}\text{H}_9$  is hydrogenated over Raney nickel to give blue-green  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_{10}\text{H}_{11}$ , which is readily oxidized in solution to the corresponding cation. Similar reactions have been carried out with 4,6,8-trimethylazulene, and the NMR spectra of the diamagnetic complexes have been assigned (70).

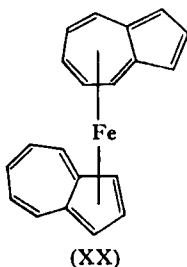
A related green, diamagnetic complex  $\text{Cr}(\text{C}_{10}\text{H}_9)_2$  is obtained from chromium(III) chloride and azulene in the presence of isopropyl Grignard reagent (58). It is assumed that the intermediate, unstable isopropylchromium(III), partially hydrogenates the azulene. The complex is assigned structure (XIX), with the chromium being attached to the seven-membered ring of one azulene, and to the five-membered ring of the other. The





three double bonds of  $\text{Cr}(\text{C}_{10}\text{H}_9)_2$  are readily hydrogenated to give the blue, diamagnetic complex  $\text{Cr}(\pi\text{-C}_{10}\text{H}_{12})_2$ , which is oxidized in solution by air to the yellow cation  $[\text{Cr}(\pi\text{-C}_{10}\text{H}_{12})_2]^+$ , isolated as its  $\text{PF}_6^-$  salt.

Use of ferric chloride in place of chromium chloride in the above reaction gives an air-stable orange diamagnetic complex  $\text{Fe}(\pi\text{-C}_{10}\text{H}_8)_2$ , bis(azulene)-iron (58). This result is surprising, as one might have expected a stable ferrocene-type of compound such as  $\text{Fe}(\pi\text{-C}_{10}\text{H}_9)_2$ , derived from the  $\text{C}_{10}\text{H}_9^-$  anion. The suggested structure (XX) indicates the complex to be formally similar to  $\text{C}_7\text{H}_8\text{FeC}_7\text{H}_{10}$  (see Section II, D).



Possibly the very much reduced air-sensitivity is due to shielding of the metal atom by the bulky substituents. The presence of five free double bonds is confirmed by hydrogenation over Raney nickel, which gives a similar air-stable complex  $\text{C}_{20}\text{H}_{26}\text{Fe}$ . Neither iron complex forms an isolable cation on oxidation.

Complexes of azulene with rhodium(III) and palladium(II) have been mentioned (19).

## III

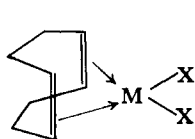
## COMPLEXES WITH EIGHT-MEMBERED RINGS AS LIGANDS

## A. Complexes of the isomeric Cyclooctadienes

Of the three isomeric cyclooctadienes, the most interesting and the most studied from the point of view of its metal complexes is the 1,5-isomer. This diolefin, when obtained by dimerizing butadiene, exists principally in the tub conformation with *cis-cis* double bonds (80, 131, 138), and is therefore ideally suited to behave as a chelate ligand. It forms very stable complexes with metals towards the ends of the transition series, especially those whose salts characteristically complex directly with olefins.

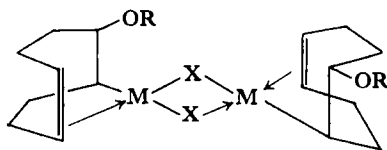
## 1. Platinum(II) and Palladium(II) complexes

The monomeric, square-planar complexes (diene) $\text{MX}_2$  (XXI) (diene = 1,5- $\text{C}_8\text{H}_{12}$ ;  $\text{M} = \text{Pd}, \text{Pt}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{or I}$ ) are formed by direct reaction of cycloocta-1,5-diene with the appropriate  $\text{Na}_2\text{MX}_4$  salts in alcoholic media (25, 26). The complex  $\text{C}_8\text{H}_{12}\text{PdCl}_2$  can also be obtained by ligand displacement from  $(\text{PhCN})_2\text{PdCl}_2$  (26). The platinum complexes are thermally stable up to  $200^\circ\text{C}$ , the stabilities decreasing in the order  $\text{Cl} > \text{Br} > \text{I}$ . On heating with methanolic sodium carbonate,  $\pi\text{-C}_8\text{H}_{12}\text{PtCl}_2$  is converted into a methoxide  $[\pi\text{-C}_8\text{H}_{12}\text{Pt}(\text{OMe})_2]_n$  of unknown structure, probably polymeric, which passes into an isomeric, dimeric complex  $(\text{C}_8\text{H}_{12}\text{OMe})_2\text{Pt}_2\text{Cl}_2$  after several days at  $-70^\circ\text{C}$  (25). The corresponding dimeric iodide is obtained directly from  $\pi\text{-C}_8\text{H}_{12}\text{PtI}_2$  and methanolic base, and other alkoxy derivatives can also be made. The halogen bridges can be cleaved by *p*-toluidine to give monomeric complexes, e.g.,  $\text{C}_8\text{H}_{12}\text{OMePtCl}(\textit{p}\text{-tol})$ . It is suggested that the elements of alcohol ( $\text{ROH}$ ) add across one double bond of the diene, with formation of a platinum-carbon  $\sigma$  bond (XXIa) (25),



(XXI)

$\text{M} = \text{Pd}, \text{Pt}$   
 $\text{X} = \text{Cl}, \text{Br}, \text{I}$

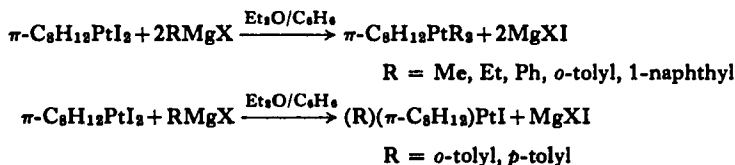


(XXIa)

$\text{R} = \text{Me}, \text{Et}, \textit{n}\text{-Pr}$

Analogous palladium complexes are known, but they are less stable than the platinum complexes, and are more readily reconverted to the (diene) $\text{MCl}_2$  complexes by concentrated  $\text{HCl}$  (26).

The iodine atoms of  $\pi\text{-C}_8\text{H}_{12}\text{PtI}_2$  can be partly or wholly replaced by alkyl and aryl groups to give colorless organoplatinum(II) complexes of considerable thermal stability (99).



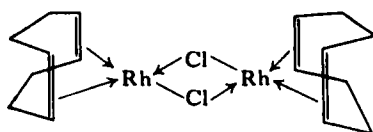
The assignment of a band at  $1428\text{ cm}^{-1}$  in these complexes to the  $\text{C}=\text{C}$  stretching frequency of the complexed diolefin (99) seems unlikely to be correct, since this band also appears in free cycloocta-1,5-diene (80).

A corresponding colorless crystalline derivative of palladium(II),  $\pi\text{-1,5-C}_8\text{H}_{12}\text{PdMe}_2$ , is obtained from  $\pi\text{-C}_8\text{H}_{12}\text{PdCl}_2$  and methyllithium at  $-40^\circ\text{C}$ , but is very much less stable than its platinum analog (22).

Nothing is known about the chelating tendencies of cycloocta-1,3-diene and cycloocta-1,4-diene with platinum(II). Methanolic  $\text{Na}_2\text{PdCl}_4$  reacts with the 1,3-diene at room temperature to give a methoxy-substituted  $\pi$ -allyl complex, while on heating  $\pi$ -cycloocta-2,4-dienylpalladium(II) chloride is formed (122). The latter is also obtained from the diene and  $\text{PdCl}_2$  in acetic acid (82). Both complexes are similar to their cyclohepta-1,3-diene analogs (Section II, D).

## 2. Complexes of Rhodium, Iridium, Ruthenium, and Osmium

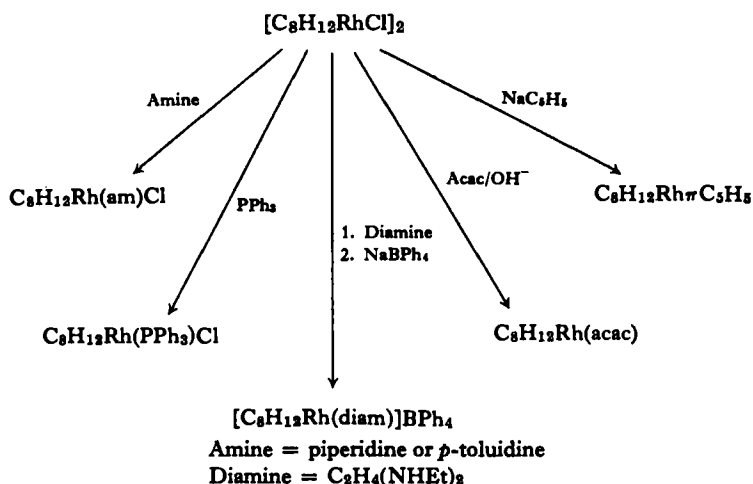
Cycloocta-1,5-diene reacts with rhodium(III) chloride in boiling ethanol to give a dimeric complex of rhodium(I),  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$  (27, 28). Reduction presumably occurs at the expense of the diolefin. The same product can be obtained in the presence of reducing agents, and by starting from rhodium(I) carbonyl chloride. Corresponding bromo, iodo, and acetato derivatives can also be made, and the usual stability order of the halogeno complexes,  $\text{I} < \text{Br} < \text{Cl}$ , is observed. X-ray study of  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$  shows the diene to be in the tub configuration; the rhodium is in square-planar coordination with the diene and two bridging chlorine atoms (XXII) (83, 84). This is as expected, since rhodium(I) ( $d^8$ ) is isoelectronic with palladium(II). There is no evidence for metal-metal interaction in the



(XXII)

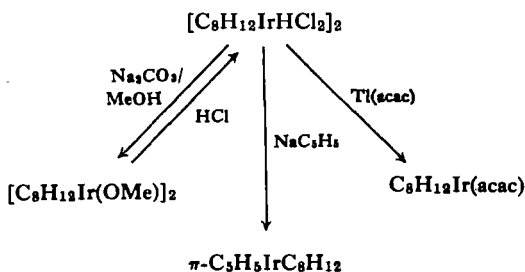
structure of  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$ , and the (diene) $\text{RhCl}_2$  units are coplanar (compare  $[\text{Rh}(\text{CO})_2\text{Cl}]_2$  (34) which has  $\text{Rh}-\text{Rh}$  bonds). The NMR spectrum of  $[\text{C}_8\text{H}_{12}\text{RhCl}]_2$  differs little from that of the free diolefin (76).

The chlorine bridges of  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$  are readily cleaved by a variety of ligands. Some of these reactions are summarized as follows:



The complex  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$  also dissolves in warm concentrated  $\text{HCl}$ , but crystallizes out again on cooling. This may be due to the formation of an acid  $\text{H}^+ [\text{C}_8\text{H}_{12}\text{RhCl}_2]^-$ , or an unstable rhodium(III) hydride  $[\text{C}_8\text{H}_{12}\text{-RhHCl}_2]_2$ . All attempts to obtain rhodium(III) complexes of cycloocta-1,5-diene by halogen oxidation of the rhodium(I) complexes have been unsuccessful. The stability of square-planar rhodium(I)-olefin complexes with respect to octahedral rhodium(III)-olefin complexes has been ascribed to the necessity of having a vacant  $p_x$  orbital on the metal to hybridize with the  $d_{xz}$  and  $d_{yz}$  orbitals for back-donation to the antibonding orbitals of the olefin (28).

The chemistry of cycloocta-1,5-diene with iridium shows interesting similarities and differences compared with its rhodium chemistry. The diolefin reacts with  $\text{H}_2\text{IrCl}_6$  in boiling ethanol to give a dimeric, halogen-bridged, hydrido diolefin complex of octahedral iridium(III),  $[\pi\text{-C}_8\text{H}_{12}\text{IrHCl}_2]_2$  in 70% yield, with a Ir—H stretching frequency at  $2261\text{ cm}^{-1}$  (123). With  $\text{Na}_2\text{IrCl}_6$  in hot aqueous ethanol, however, the orange-red iridium(I) complex  $[\pi\text{-C}_8\text{H}_{12}\text{IrCl}]_2$ , analogous to  $[\pi\text{-C}_8\text{H}_{12}\text{RhCl}]_2$ , is formed (136); this adds HCl to give the iridium(III) hydride. Treatment of the hydride with basic reagents forms iridium(I) complexes (123), e.g.,



In the presence of stannous chloride, cycloocta-1,5-diene reacts with  $\text{Na}_2\text{IrCl}_6$  to give a yellow complex  $(\pi\text{-C}_8\text{H}_{12})_2\text{IrSnCl}_3$ , which presumably contains five-coordinate iridium(I) attached to two diene molecules and a  $\text{SnCl}_3^-$  group (137). Treatment with triphenylphosphine displaces one of the diolefin molecules giving a monomeric five-coordinate species  $\pi\text{-C}_8\text{H}_{12}\text{-Ir}(\text{Ph}_3\text{P})(\text{SnCl}_3)$ . The  $\text{SnCl}_3$  group in  $(\pi\text{-C}_8\text{H}_{12})_2\text{IrSnCl}_3$  is readily ionized in dimethylformamide, and the presumably square-planar  $[(\pi\text{-C}_8\text{H}_{12})_2\text{Ir}]^+$  cation can be precipitated as its  $\text{BPh}_4^-$  salt.

Ruthenium(III) chloride in ethanol reacts with cycloocta-1,5-diene to give an insoluble, brown ruthenium(II) complex  $[\pi\text{-C}_8\text{H}_{12}\text{RuCl}_2]_n$  (12), which is probably an octahedral, halogen-bridged polymer (4). Analogous bromo and iodo complexes can also be made. The halogen bridges are split by *p*-toluidine to give complexes such as  $\pi\text{-C}_8\text{H}_{12}\text{Ru}(\text{p-tol})_2\text{Cl}_2$ .

Only one osmium complex of this type is known. The osmium(II) complex  $[\text{Os}_2\text{Cl}_3(\text{PPh}_2\text{Et})_6]\text{Cl}$ , containing three bridging chlorine atoms, is reported to react with cycloocta-1,5-diene to give presumably octahedral  $\pi\text{-C}_8\text{H}_{12}\text{Os}(\text{PPh}_2\text{Et})_2\text{Cl}_2$  (24).

The strong tendency of cycloocta-1,5-diene to form chelate complexes is emphasized by the observation that rhodium(III) chloride reacts with

cycloocta-1,3-diene to give the rhodium(I) complex of the 1,5-diene (121). This isomerization to the thermodynamically less favored diolefin may proceed via unstable rhodium hydride intermediates. Rinehart and Lasky (121) failed to observe any of the 1,4-isomer during the isomerization, and they conclude that there is a rapid hydrogen transfer from the 5,6- to the 3,4-position of the 1,3-diene via a  $\pi$ -allyl hydrido intermediate. A similar isomerization occurs, though more slowly, with ruthenium(II) and iridium(III) halides (121), and with ruthenium- and iridium-stannous chloride complexes (137).<sup>2a</sup>

### 3. Complexes of Copper, Silver, and Gold

Copper- and silver-olefin complexes are usually thermally unstable, and their composition can vary even with a given olefin (10, 77). Frequently, they are not stable enough to be isolated. As expected, however, cycloocta-1,5-diene forms very stable complexes with copper(I) and silver(I). The copper(I) complexes  $\pi$ -C<sub>8</sub>H<sub>12</sub>·CuX (X = Cl, Br) are prepared as colorless solids either by direct reaction of cuprous halide with the diene (79, 80, 125), or by SO<sub>2</sub> reduction of the cupric halide with the diene (78). A suggestion (80), based on the infrared spectrum, that  $\pi$ -C<sub>8</sub>H<sub>12</sub>·CuCl contains the diene in a chair conformation has been refuted by the X-ray study (79), which shows the diene in its preferred boat conformation. The molecule is dimeric with halogen bridges, the copper being tetrahedrally coordinated. The heat of dissociation of [C<sub>8</sub>H<sub>12</sub>·CuCl]<sub>2</sub> is reported as 23.5 kcal/mole (100). This complex is also reported to catalyze the dimerization of cycloocta-1,5-diene in 30% yield to tricyclo[3.3.0.0<sup>2,6</sup>]octane (127). The colorless silver nitrate complex 1,5-C<sub>8</sub>H<sub>12</sub>·AgNO<sub>3</sub> (33, 86) is more stable than the complexes C<sub>8</sub>H<sub>12</sub>·2AgNO<sub>3</sub> formed by the 1,3- and 1,4-dienes (86), but there are no structural data. Cycloocta-1,3-diene also forms an unstable copper(I) complex C<sub>8</sub>H<sub>12</sub>·3CuCl (78).

Conflicting reports on gold complexes of cycloocta-1,5-diene have recently appeared. Chalk (23) describes colorless complexes of gold(I), C<sub>8</sub>H<sub>12</sub>·2AuCl, and gold(III), C<sub>8</sub>H<sub>12</sub>·AuCl<sub>3</sub>, whereas Hüttel and Dietl (81) report a yellow gold(I) complex [C<sub>8</sub>H<sub>12</sub>·AuCl]<sub>n</sub>.

<sup>2a</sup> Note added in proof: In the preparation of rhodium and iridium complexes from cycloocta-1,5-diene, however, all the *uncomplexed* olefin is converted to the 1,3-diene. The same isomerization is catalyzed by tertiary phosphine complexes of rhodium and iridium, and the 1,4-diene can be detected as an intermediate (117a).

#### 4. Reaction of Cyclooctadienes with Metal Carbonyls

Nearly all published work on this topic relates to cycloocta-1,5-diene. This diolefin readily displaces two CO groups from the Group VI hexacarbonyls on heating, giving yellow, diamagnetic, monomeric substitution products of formula  $\pi$ -1,5- $C_8H_{12}M(CO)_4$  ( $M = Cr, Mo, W$ ) (12, 52, 103). These show three or four CO stretching frequencies in the infrared, as expected for an octahedral *cis*-disubstituted tetracarbonyl, and the dipole moment of the molybdenum complex is 4.88 D (52). Its NMR spectrum is not greatly different from that of the free diolefin (12). [Compare NMR spectra of conjugated diene iron tricarbonyls (118).<sup>3</sup>]

Cycloocta-1,5-diene is quantitatively isomerized to the 1,3-isomer on heating with  $Fe(CO)_5$  (8), and it is possible that an unstable yellow oil obtained by reaction between  $Fe(CO)_5$  or  $Fe_3(CO)_{12}$  and the 1,5-diene, and formulated as  $\pi$ -1,5- $C_8H_{12}Fe(CO)_3$  (94, 114), may in fact be  $\pi$ -1,3- $C_8H_{12}Fe(CO)_3$ . As pointed out by Pettit and Emerson (118), the instability of the complex could be due to the ring strain involved in making the double bonds of the 1,3-diene coplanar.

The complex  $\pi$ - $C_5H_5Co(CO)_2$ , which is formally isoelectronic with  $Fe(CO)_5$ , readily forms crystalline, orange, sublimable  $\pi$ - $C_5H_5Co$ - $\pi$ - $C_8H_{12}$  on heating with cycloocta-1,5-diene (97, 115, 116). NMR studies show that the 1,5-isomer is coordinated to the metal. Clearly the oxidation state of the metal is an important factor in determining the type of olefin complex formed. The cobalt(I) complex is analogous to the rhodium(I) and iridium(I) complexes  $\pi$ - $C_5H_5M$ - $\pi$ - $C_8H_{12}$  obtained from the compounds [ $\pi$ - $C_8H_{12}MCl$ ]<sub>2</sub> and  $NaC_5H_5$  (q.v.).

The behavior of cycloocta-1,5-diene with  $\pi$ - $C_5H_5Mn(CO)_3$  is quite different. Heating and irradiation of the mixture gives a yellow, insoluble, air-stable complex  $C_8H_{12}[\pi$ - $C_5H_5Mn(CO)_2$ ]<sub>2</sub>, in which the diene is behaving as a bridging, rather than as a chelate, diolefin (53). No trace of the expected  $\pi$ - $C_5H_5Mn(CO)(\pi$ - $C_8H_{12})$  can be isolated. It may be noted that other bidentate ligands do not readily form chelate substitution products with  $\pi$ - $C_5H_5Mn(CO)_3$  (53).

Cycloocta-1,5-diene does not displace CO groups from nickel carbonyl (28), although in the presence of certain quinones, air-stable, diamagnetic complexes of the type  $C_8H_{12}Ni$ (quinone) can be isolated. These have been

<sup>3</sup> For a review of the NMR spectra of organometallic compounds, see the chapter by M. L. Maddox, S. L. Stafford, and H. D. Kaesz, *Advan. Organomet. Chem.* 3, 1 (1965).

reviewed by Schrauzer (124). An X-ray study of  $\pi$ -C<sub>8</sub>H<sub>12</sub>Ni(duroquinone) shows an essentially tetrahedral configuration about the metal, with the eight-membered ring in its usual boat (or tub) conformation (74). The double-bond lengths of the diene in the complex (1.33 Å) are practically equal to those in the free diene.

The complex Ni( $\pi$ -1,5-C<sub>8</sub>H<sub>12</sub>)<sub>2</sub>, presumably a tetrahedral complex of Ni(0), has been obtained as air-sensitive, yellow crystals by ligand displacement from Ni(cyclododecatriene), or by reducing nickel acetylacetonate with alkyl aluminums in the presence of the diene (133). Derivatives such as C<sub>8</sub>H<sub>12</sub>Ni(acac) and C<sub>8</sub>H<sub>12</sub>Ni(PPh<sub>3</sub>)<sub>2</sub> have also been mentioned (134). This work is summarized elsewhere (124).

### B. Complexes of Cyclooctatetraene

Of all the eight-membered rings, cyclooctatetraene is potentially the most interesting from the point of view of its metal complexes, because there are so many ways in which it could conceivably bond to a transition metal. The free olefin exists in the tub conformation, with effectively no conjugation between the double bonds (120). It can be reduced by alkali metals, or at the dropping mercury electrode, to the planar cyclooctatetraenyl dianion, C<sub>8</sub>H<sub>8</sub><sup>2-</sup>, which has 10  $\pi$  electrons, and would be expected to behave as an aromatic system according to Hückel's Rule. Infrared, NMR, and ultraviolet spectroscopic studies on K<sub>2</sub>C<sub>8</sub>H<sub>8</sub>·THF support this conclusion (67, 88).

The following possibilities (Fig. 1) can therefore be considered for the bonding of cyclooctatetraene in metal complexes:

(1) In the tub conformation, it could coordinate via the 1,5-double bonds, like cycloocta-1,5-diene, two double bonds being not involved (Fig. 1a). It could also act as a bridging group, the 1,5- and 3,7-double bonds being coordinated to two metal atoms (Fig. 1b).

(2) It could form mononuclear diene complexes in which one planar diene unit is attached to a metal atom (as in butadieneiron tricarbonyl) (Fig. 1c), or could behave as a bridging group with two diene units each attached to two metal atoms (Fig. 1d). In these cases, the conformation of the olefin need no longer be tub.

(3) It could form complexes in which six of the eight available  $\pi$  electrons are used in bonding to a transition metal, as in (cycloheptatriene)Cr(CO)<sub>3</sub>.



This might involve the hypothetical valence tautomer of cyclooctatetraene, bicyclo[3.2.0]octa-2,4,7-triene (Fig. 1e).

(4) Cyclooctatetraene could form "sandwich" or, more likely, "half-sandwich" complexes in which the 10  $\pi$  electrons of the planar dianion  $C_8H_8^{2-}$  are involved in bonding to a transition metal (Fig. 1f).

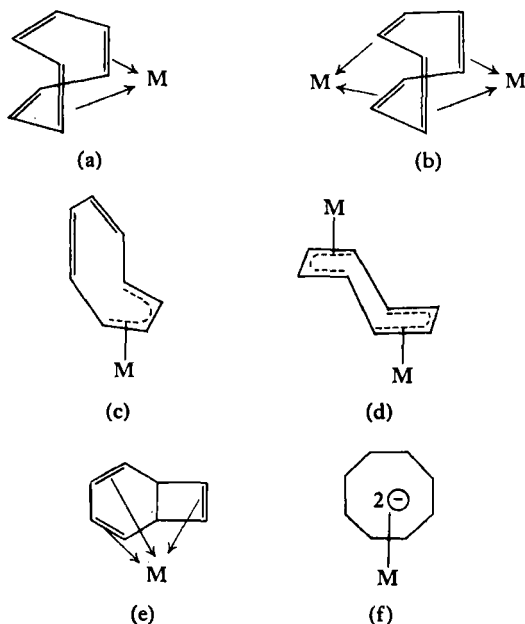


FIG. 1. Some possibilities for the bonding of cyclooctatetraene to transition metals.

It seems likely that in most of the cyclooctatetraene complexes so far prepared the olefin is in its usual tub conformation, the only notable exception being the iron tricarbonyl complexes (40, 41, 42).

Three silver complexes,  $2C_8H_8 \cdot AgNO_3$ ,  $C_8H_8 \cdot AgNO_3$ , and  $2C_8H_8 \cdot 3AgNO_3$ , can be isolated from the reaction of cyclooctatetraene with silver nitrate under various conditions (31). An X-ray study of the 1:1 adduct shows the olefin in the tub conformation coordinated via the 1,5-double bonds to a silver ion, the  $Ag-C_8H_8$  units being held in infinite chains by a weaker intermolecular interaction between the formally uncoordinated bonds and silver ions (106, 107). The solid-state infrared spectrum shows a band at  $1449\text{ cm}^{-1}$  which is assigned as a complexed  $C=C$  stretching frequency, but there is no band due to the uncoordinated, or more weakly

coordinated, C=C frequency (69). Surprisingly, there is only one proton resonance signal at 4.3  $\tau$  in benzonitrile, instead of the expected two due to the coordinated and uncoordinated olefinic protons.

Cuprous chloride or bromide react with cyclooctatetraene to give adducts of the type  $C_8H_8 \cdot 2CuCl$  and  $C_8H_8 \cdot CuBr$ , respectively, whose infrared spectra show free and uncoordinated C=C stretching frequencies (125). A second adduct with cuprous chloride,  $C_8H_8 \cdot CuCl$ , is made by reducing cupric chloride with sulfur dioxide in the presence of the olefin (78). An X-ray study shows the structure of this complex to be similar to that of  $C_8H_8 \cdot AgNO_3$ , the olefin being in the tub conformation (9).

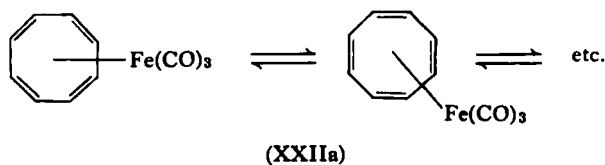
The cyclooctatetraene complexes of platinum(II),  $\pi-C_8H_8PtX_2$  ( $X = Cl, Br, I$ ) were among the first complexes of chelate diolefins known. They are made from the reaction of cyclooctatetraene with platinum(II) halogeno salts at room temperature (85), but owing to their poor solubility in organic solvents, relatively few physical measurements have been carried out on them. The analogous complexes  $\pi-C_8H_8PdX_2$  ( $X = Cl, Br$ ) have also been made (69, 73). Fritz and Keller (69) state that  $\pi-C_8H_8PdCl_2$  and  $\pi-C_8H_8PtI_2$  show no band assignable to a free C=C stretching frequency in their solid-state infrared spectra, and conclude from the simplicity of the infrared spectra that the tub form of the ring cannot be present. Further, the NMR spectrum of  $\pi-C_8H_8PdCl_2$  shows only one signal in solvents such as dimethylformamide and benzonitrile. The authors conclude that in the platinum and palladium complexes the ring must be planar, or nearly so. However, it is always possible that polar solvents could displace the cyclooctatetraene from its metal complexes, giving rise to the one proton resonance of the free olefin and experience with  $\pi$ -complexes such as  $\pi-C_8H_8AgNO_3$ ,  $\pi-C_8H_8Fe(CO)_3$ , and  $\pi-C_5H_5V-\pi-C_7H_7$  argues against dogmatic assertions of structure based only on infrared spectra. It must also be noted that other workers report  $\pi-C_8H_8PtI_2$  to show a weak band at about  $1635\text{ cm}^{-1}$ , which could be a C=C stretching frequency (99). A tub conformation of  $C_8H_8$  in the platinum and palladium complexes seems most likely.

The complex  $\pi-C_8H_8PtI_2$  reacts with alkyl and aryl Grignard reagents to give mononuclear complexes such as  $\pi-C_8H_8PtMe_2$ ,  $\pi-C_8H_8PtEtI$ , and  $\pi-C_8H_8Pt(p\text{-tolyl})_2$ , similar to those formed from cycloocta-1,5-diene, and also binuclear complexes such as  $\pi-C_8H_8Pt_2Me_4$  and  $\pi-C_8H_8Pt_2Ph_4$  (45, 99). The mononuclear complexes show a C=C stretching frequency at  $1635\text{ cm}^{-1}$  which is absent from the binuclear complexes, and the latter probably contain the tub form of the olefin bridging two platinum atoms.

Cyclooctatetraene is readily displaced from its platinum complexes by  $\sigma$ -donor ligands such as pyridine and triphenylphosphine.

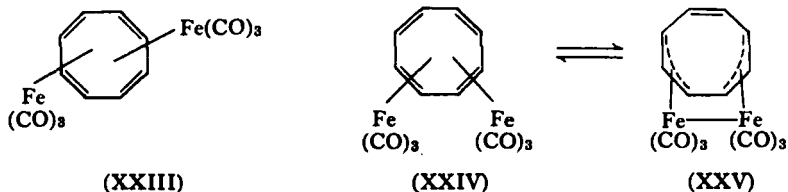
A thermally unstable complex of rhodium(I),  $[\pi\text{-C}_8\text{H}_8\text{RhCl}]_2$ , prepared from ethanolic rhodium(III) chloride and cyclooctatetraene, shows two proton resonance lines at 5.8  $\tau$  and 4.3  $\tau$  in carbon disulfide, and probably also contains the tub form of the olefin (13).

Cyclooctatetraene forms a number of interesting complexes in its reactions with metal carbonyls. The structures and reactions of  $\pi\text{-C}_8\text{H}_8\text{Fe}(\text{CO})_3$  and  $\pi\text{-C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  have been discussed in detail by Pettit and Emerson (118). These complexes represent the only examples in which conformations other than tub (chair, in these cases) have been definitely established for cyclooctatetraene in its metal complexes. There seems to be little doubt that, in solution,  $\pi\text{-C}_8\text{H}_8\text{Fe}(\text{CO})_3$  is undergoing valence tautomerism, with the  $\text{Fe}(\text{CO})_3$  group rotating rapidly about the ring (XXIIa),



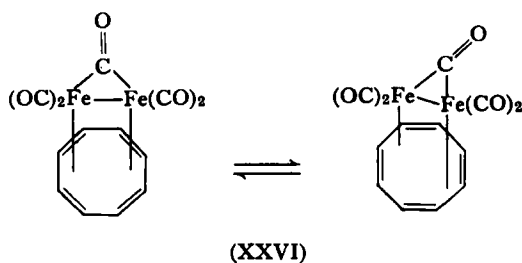
leading to equivalence of the ring protons in the NMR spectrum, and an effectively planar  $\text{C}_8$  ring. However, it is still not clear why the solid-state infrared spectrum of  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$  should show no free  $\text{C}=\text{C}$  stretching frequency.<sup>3a</sup>

Pettit and co-workers (89) have recently isolated three isomeric complexes of formula  $\pi\text{-C}_8\text{H}_8\text{Fe}_2(\text{CO})_6$  from the reaction of  $\text{Fe}_2(\text{CO})_9$  with cyclooctatetraene. One is identical with the known compound obtained from  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_3(\text{CO})_{12}$  and the olefin, with a *trans* configuration of  $\text{Fe}(\text{CO})_3$  groups (40). The second is the *cis* isomer (XXIV) with the  $\text{Fe}(\text{CO})_3$  groups on the same side of the ring in its chair conformation, as shown by the NMR



<sup>3a</sup> Note added in proof: For a more detailed study of the vibrational spectra of  $\text{C}_8\text{H}_8\text{Fe}(\text{CO})_3$  see: R. T. Bailey, E. R. Lippincott, and D. Steele, *J. Am. Chem. Soc.* **87**, 5346 (1965).

spectrum and the dipole moment (3.9 D). The third isomer, which is in thermal equilibrium with the second in solution, is formulated as a bis( $\pi$ -allyl) complex (XXV) similar to the iron complexes obtained with cycloheptatriene (Section II, A) and cyclooctatriene (Section III, C). On standing, the two new isomers lose CO and form a black complex  $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>5</sub>, which shows a bridging CO frequency at 1803 cm<sup>-1</sup> and is evidently identical with a complex formulated previously as  $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>7</sub> (102). Unlike the  $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub> isomers, this complex shows only one proton resonance signal in solution, presumably owing to valence tautomerism in solution with rapid rotation of the iron-iron bond about the ring (XXVI).



It is of interest that cobalt(I), which is isoelectronic with iron(0), does not stabilize the chair conformations of the cyclooctatetraene ring as found in  $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub> and *trans*- $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe<sub>2</sub>(CO)<sub>6</sub>. The complex  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub> reacts with cyclooctatetraene to give a poor yield of brown, crystalline  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co- $\pi$ -C<sub>8</sub>H<sub>8</sub> (113, 117). A tub conformation of the eight-membered ring is suggested by the appearance of a "free" C=C stretching frequency at 1626 cm<sup>-1</sup>, and by the appearance of two proton resonance signals due to the coordinated and uncoordinated olefinic protons. Unlike  $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub>,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co- $\pi$ -C<sub>8</sub>H<sub>8</sub> can readily be hydrogenated (117), and does not add on tetracyanoethylene (39). It can be protonated by fluoroboric acid to give a cyclooctatrienium species [ $\pi$ -C<sub>5</sub>H<sub>5</sub>Co- $\pi$ -C<sub>8</sub>H<sub>9</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, but this is very unstable compared with the corresponding iron(0) species [ $\pi$ -C<sub>8</sub>H<sub>8</sub>Fe(CO)<sub>3</sub>]<sup>+</sup>BF<sub>4</sub><sup>-</sup>, presumably because the positive charge cannot be delocalized in the  $\pi$  orbitals of the ring in its tub conformation (39).

A red-brown, binuclear complex  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co- $\pi$ -C<sub>8</sub>H<sub>8</sub>- $\pi$ -Co- $\pi$ -C<sub>5</sub>H<sub>5</sub> is also formed in the reaction of  $\pi$ -C<sub>5</sub>H<sub>5</sub>Co(CO)<sub>2</sub> with cyclooctatetraene (68), and on the basis of its infrared spectrum the presence of a planar C<sub>8</sub>H<sub>8</sub> ring bridging two cobalt atoms has been inferred. The analogous rhodium(I) complexes,  $\pi$ -C<sub>5</sub>H<sub>5</sub>Rh- $\pi$ -C<sub>8</sub>H<sub>8</sub> and  $\pi$ -C<sub>5</sub>H<sub>5</sub>Rh- $\pi$ -C<sub>8</sub>H<sub>8</sub>- $\pi$ -Rh- $\pi$ -C<sub>5</sub>H<sub>5</sub>,

have been prepared from the reaction of  $\pi\text{-C}_8\text{H}_5\text{Rh}(\text{CO})_2$  and cyclooctatetraene (17, 39). Their NMR spectra strongly support the assumption of a tub conformation for the cyclooctatetraene ring in both complexes.

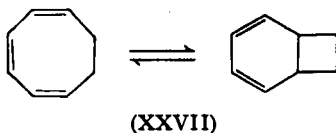
Two complexes of zero-valent nickel with cyclooctatetraene,  $\text{Ni}(\text{C}_8\text{H}_8)_2$  and  $[\text{NiC}_8\text{H}_8]_n$ , have been reported briefly (124).

No examples of cyclooctatetraene behaving as a six- $\pi$ -electron donor, possibility (3) of those listed above, have been reported.<sup>4</sup> The only complex isolated from the reaction of  $\text{Mo}(\text{CO})_6$  with cyclooctatetraene has the formula " $(\text{C}_8\text{H}_8)_2\text{Mo}(\text{CO}_4)$ ," and seems to contain a dimer of cyclooctatetraene (11, 12).

There are also no proven examples of "sandwich" complexes of the cyclooctatetraenyl dianion,  $\text{C}_8\text{H}_8^{2-}$ . On the basis of the Rare Gas Rule, such compounds might be expected to occur with the early transition metals. Cyclooctatetraene is reported to react with titanium tetrabutoxide and triethylaluminum to give the complexes  $\text{Ti}_2(\text{C}_8\text{H}_8)_4$  and  $\text{Ti}_2(\text{C}_8\text{H}_8)_3$  as black and yellow crystals, respectively (134). A brown complex  $\text{Mn}_2(\text{C}_8\text{H}_8)_3$  has also been made starting from manganous acetylacetonate. There is no structural information on these interesting compounds.

### C. Complexes of the Isomeric Cyclooctatrienes

A mixture of cycloocta-1,3,5-triene and cycloocta-1,3,6-triene formed by partial reduction of cyclooctatetraene is the usual starting point for the study of cyclooctatriene complexes, and obviously complexes may be derived from both isomers. Also, the 1,3,5-isomer is in thermal equilibrium with its valence tautomer, bicyclo[4.2.0]octa-2,4-diene (XXVII), at 100° C (30), from which complexes may also be formed. Although silver nitrate



<sup>4</sup> Note added in proof: The complex  $\pi\text{-C}_8\text{H}_8\text{Mo}(\text{CO})_3$  has recently been obtained as red crystals from the reaction of cyclooctatetraene with (diglyme) $\text{Mo}(\text{CO})_3$  (136a), and the tungsten analog has been prepared similarly from  $(\text{MeCN})_3\text{W}(\text{CO})_3$  (93a). The NMR spectrum of the molybdenum complex shows a broad line at 6.05  $\tau$  at 30°, which sharpens to a singlet at 80° and becomes more complex at -30°, presumably owing to valence tautomerism. The complex can be protonated in concentrated sulfuric acid to give the cation  $[\text{C}_8\text{H}_9\text{Mo}(\text{CO})_3]^+$ , whose NMR spectrum is interpreted to show the presence of the homotropylium ion attached to the metal atom.

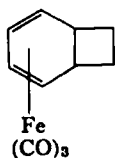
complexes of the 1,3,5- and 1,3,6-isomers,  $1,3,5\text{-C}_8\text{H}_{10}\cdot\text{AgNO}_3$  and  $1,3,6\text{-C}_8\text{H}_{10}\cdot 3\text{AgNO}_3$ , have been prepared (31, 87), their structures are unknown.

Cycloocta-1,3,5-triene can obviously behave as a six- $\pi$ -electron donor like cycloheptatriene. The isomeric cyclooctatriene mixture reacts with  $\text{Cr}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  to give orange-red complexes of formula  $\pi\text{-C}_8\text{H}_{10}\text{M}(\text{CO})_3$  ( $\text{M} = \text{Cr}, \text{Mo}$ ), which are similar to, though less stable than, the cycloheptatriene analogs; their infrared spectra show three strong C—O frequencies (59, 61).<sup>5</sup> An X-ray study of the chromium complex shows a structure similar to that of (cycloheptatriene) $\text{Mo}(\text{CO})_3$ , the six olefinic carbon atoms being almost coplanar (7). Unlike the cycloheptatriene complexes, the cyclooctatriene complexes do not react with trityl fluoroborate, and no derivatives of  $\text{C}_8\text{H}_8^{2+}$  can be isolated (61).

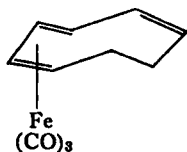
Cycloocta-1,3,5-triene also behaves similarly to cycloheptatriene in other complexes. The brown, air-sensitive compound  $\pi\text{-C}_5\text{H}_5\text{Cr-}\pi\text{-C}_8\text{H}_{10}$  ( $\mu_{\text{eff}} = 1.69$  B.M.) is prepared similarly to its cycloheptatriene analog (55). Diamagnetic complexes of formula  $\pi\text{-C}_8\text{H}_{10}\text{M-}\pi\text{-C}_8\text{H}_{12}$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) can be obtained by treating iron or ruthenium trichloride with a 1:1 mixture of cycloocta-1,3,5-triene and cycloocta-1,5-diene in the presence of isopropyl Grignard reagent in yields of 13% and 6%, respectively (54, 56). The red iron compound, which is formally analogous to  $\pi\text{-C}_7\text{H}_8\text{Fe-}\pi\text{-C}_7\text{H}_{10}$  (Section II, D), is much more air-sensitive than the yellow ruthenium compound. A colorless osmium(0) analog could not be isolated in a pure state. It is interesting that the same complexes are formed, albeit in lower yields, by starting with cycloocta-1,5-diene only. Evidently the intermediate alkyl iron compounds readily abstract hydrogen from the diene.

The behavior of the cyclooctatrienes as four- $\pi$ -electron donors is complicated by the existence and ready interconversion of the various isomers. Early work on the cyclooctatrieneiron carbonyls has been summarized (118). The yellow oil produced in the  $\text{Fe}(\text{CO})_5$ -isomeric cyclooctatriene reaction, and initially formulated as  $\pi\text{-1,3,6-C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$  (61), is now known to be (bicyclo[4.2.0]octa-2,4-diene) $\text{Fe}(\text{CO})_3$  (XXVIII) on the basis of chemical and NMR studies (104, 105, 108, 116). A less stable isomer formed from  $\text{Fe}(\text{CO})_5$  or  $\text{Fe}_3(\text{CO})_{12}$  and the isomeric trienes is formulated as  $\pi\text{-1,3,5-C}_8\text{H}_{10}\text{Fe}(\text{CO})_3$ , with coordination from a pair of conjugated double bonds (XXIX) (105, 108, 116).

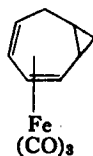
<sup>5</sup> Note added in proof: The tungsten analog,  $\pi\text{-C}_8\text{H}_{10}\text{W}(\text{CO})_3$  has recently been prepared by reaction of the 1,3,5-triene with  $(\text{MeCN})_3\text{W}(\text{CO})_3$  (93a).



(XXVIII)



(XXIX)

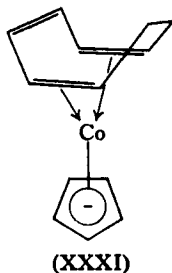


(XXX)

A third isomer of  $C_8H_{10}Fe(CO)_3$  is obtained from  $\pi-C_8H_8Fe(CO)_3$  by protonation and subsequent hydride reduction; this is formulated as (bicyclo[5.1.0]octa-2,4-diene) $Fe(CO)_3$  (XXX) (39).

A third product of the iron carbonyl-cyclooctatriene reaction is a red complex of formula  $C_8H_{10}Fe_2(CO)_6$ , which was initially formulated as  $C_9H_{12}Fe_2(CO)_6$  (61). This is derived from the 1,3,5-isomer and probably has a bis( $\pi$ -allyl) structure like the corresponding complexes with cycloheptatriene (Section II, A) and cyclooctatetraene (Section III, B) (46, 90).

The cyclooctatriene mixture also reacts with  $\pi-C_5H_5Co(CO)_2$  to give two isomers of formula  $\pi-C_5H_5Co-\pi-C_8H_{10}$  (97, 108, 117). In this case, the less stable isomer, a red solid m.p.  $46^\circ C$ , is derived from bicyclo[4.2.0]octa-2,4-diene, while the more stable isomer, a yellow solid m.p.  $98^\circ C$ , is derived from cycloocta-1,3,5-triene. NMR studies show that, in the latter complex, coordination takes place via a pair of unconjugated, chelate double bonds, the olefin being in a tub conformation (XXXI). In agreement with this, the protonated species is very unstable. This work, and the related studies on



(XXXI)

$C_8H_8$  and  $C_8H_{12}$  complexes, show the clear preference of the  $\pi-C_5H_5Co$  group compared with the  $Fe(CO)_3$  group for chelate rather than conjugated diolefins.

The cyclooctatrienes can also behave as four- $\pi$ -electron donors in their Group VI complexes. The isomeric mixture of trienes reacts with  $Mo(CO)_6$  to give an air-stable, yellow complex  $(\pi-C_8H_{10})_2Mo(CO)_2$  in addition to

the complex  $\pi$ -1,3,5- $\text{C}_8\text{H}_{10}\text{Mo}(\text{CO})_3$ , and the yellow complex  $(\pi\text{-C}_8\text{H}_{10})_2\text{W}(\text{CO})_2$  is the only isolated product from the reaction with  $\text{W}(\text{CO})_6$  (59, 61). From the infrared spectra it has been concluded that these complexes contain the 1,3,6-isomer, and this is supported by the observation that  $(\pi\text{-C}_8\text{H}_{10})_2\text{Mo}(\text{CO})_2$  is the only product of reaction of  $\text{Mo}(\text{CO})_6$  and pure cycloocta-1,3,6-triene. However, the reported infrared spectra show no band characteristic of a  $\text{C}=\text{C}$  stretching frequency, and in view of the ready isomerizations of olefins by metal carbonyls, the assignment cannot be certain. The dicarbonyl complexes show three CO frequencies in their solid-state infrared spectra which, together with the observed dipole moment of  $1.96 \pm 0.05$  D for  $(\pi\text{-C}_8\text{H}_{10})_2\text{Mo}(\text{CO})_2$ , indicates a *cis* configuration.

A yellow, air-stable complex  $[\pi\text{-C}_8\text{H}_{10}\text{Co}(\text{CO})_2]_2$  is obtained from the reaction of the triene mixture with cobalt carbonyl (60). The infrared spectrum was interpreted to show the presence of the 1,3,6-isomer in the complex.

The eight-membered ring ketone, cyclooctatrienone,  $\text{C}_8\text{H}_8\text{O}$ , forms some iron carbonyl complexes similar to those formed by cycloocta-1,3,5-triene. The yellow complex  $(\pi\text{-C}_8\text{H}_8\text{O})\text{Fe}(\text{CO})_3$  shows no  $\text{C}=\text{O}$  frequency in the range normal for strained-ring ketones (about  $1775\text{ cm}^{-1}$ ), and probably contains the 1,3,5-trienone as ligand, not the bicyclic isomer (90). The orange, binuclear compound  $(\pi\text{-C}_8\text{H}_8\text{O})\text{Fe}_2(\text{CO})_6$  is probably a bis( $\pi$ -allyl) complex. However, cyclooctatrienone does not form tricarbonyl complexes with the Group VI metals (cf., tropone and cycloheptatriene), presumably owing to the difficulty of making the three double bonds coplanar.

#### D. Complexes of Cyclooctene

Distribution measurements show that the silver complex of *cis*-cyclooctene is less stable than that of cycloheptene, presumably owing to more ring strain in the latter (129, 130). *trans*-Cyclooctene is considerably more strained than the *cis* isomer, and can be separated from it by extraction with 20% aqueous silver nitrate (32), but there are no quantitative measurements of the stability of the silver complex of the *trans* isomer. The interesting possibility of isomerizing *cis* to *trans*-cyclooctene via metal complexes has not yet been achieved. *trans*-Cyclooctene has been resolved via its platinum(II) complex with the optically active amine 1-phenyl-2-amino-propane (am),  $\pi\text{-C}_8\text{H}_{14}\text{PtCl}_2\text{am}$ . (29).



The brown, insoluble complex of cyclooctene with  $\text{PdCl}_2$ ,  $[\pi\text{-C}_8\text{H}_{14}\text{PdCl}_2]_2$ , is remarkably stable, and, unlike the analogous cycloheptene complex, cannot be converted into a  $\pi$ -allyl complex on heating (82). 1-Methylcyclooctene gives a similar olefin complex, but, on heating, this is converted into a yellow  $\pi$ -allyl complex, which is shown by NMR to have the *exo* structure analogous to that of the corresponding 1-methylcycloheptene complex (Section II, E).<sup>6</sup>

A yellow, air-stable complex  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{-}\pi\text{-C}_8\text{H}_{14}$  has been reported from the reaction of *cis*-cyclooctene with  $\pi\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$  (53). There was no isomerization to the *trans* isomer, as is observed in the corresponding cyclononene complexes.

<sup>6</sup> Note added in proof: A rhodium(I) complex of cyclooctene,  $\pi\text{-C}_8\text{H}_{14}\text{RhCl}$ , has recently been reported (118a). It is presumably dimeric.

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